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REYNOLDS'S
EXPERIMENTAL CHEMISTRY.
PART. III.
METALS AND ALLIED BODIES



EXPERIMENTAL CHEMISTRY

FOR

JUNIOR STUDENTS.

BY

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PART III.

METALS AND ALLIED BODIES

(with an Analytical Appendix).

LONDON :

LONGMANS, GREEN, AND CO.

1884.

1934. f. 4c.



LONDON : PRINTED BY
SPOTTISWOODE AND CO., NEW-STREET SQUARE
AND PARLIAMENT STREET

PREFACE.

THE success which has attended the issue of Parts I. and II. of this work leads the author to hope that the present volume, which continues the same line of study, may also prove useful to a large class of students. His aim in this Part, as in its predecessors, is to place the student to some extent in the position of an independent investigator of chemical phenomena. This consideration has largely influenced the *order* of study pursued, which, though somewhat unusual in dealing with the metals and allied bodies, seems best adapted to lead the worker to recognise the natural affinities of the elements, as well as their distinctive characters.

Detailed descriptions of metallurgical processes would be obviously foreign to the character of the work, but an outline of each of the more important operations is given, and illustrative experiments are added whenever they are likely to elucidate the general statement.

The author trusts that the Analytical Appendix will be found equally useful to advanced as well as to junior students. The Synoptic Tables included in the Appendix have been employed with advantage for some years in the Dublin University Laboratory. They were arranged by the author with a view to enable students to *compare* the reactions of the metals, and to aid in planning methods for their recognition in simple and in complex mixtures presented for analysis. The ready-made tables often given for the separation of the metals, though generally good, possess little educational value, and their use often produces unintelligent analysts; whereas the gradual development of such schemes by *the student* for himself is a most useful intellectual exercise. A special table for the analysis of a solution containing but one metal is given as an illustration of the many schemes which may be devised for similar purposes.

J. E. R.

TRINITY COLLEGE,
DUBLIN UNIVERSITY.

CONTENTS.

CHAPTER XXVI.

	PAGE
Experiments with arsenic and its compounds—Reduction of arsenic—Oxides—Arsenious and arsenic acids—Law of isomorphism—Chorides, hydride, &c., tests for—Arsenical wall-paper—Poisoning, antidotes	1

CHAPTER XXVII.

Experiments with antimony and its compounds—Antimony, its reduction—Chlorides, oxides, and acids—Tartar emetic—Sulphides—Tests—Poisoning, antidotes	25
---	----

CHAPTER XXVIII.

Experiments with bismuth and its compounds—Bismuth, fusible metal—Nitrates, oxides, carbonate, chloride, &c.—Sulphide—Tests—Rare elements: vanadium, tantalum, and niobium	38
--	----

CHAPTER XXIX.

Experiments with tin and its compounds—Tinstone—Reduction—Alloys—Stannous and stannic compounds—Uses of tin salts in dyeing—Mordants— <i>Aurum musivum</i> —Tests—Rare metals: titanium, thorium, and zirconium	48
---	----

CHAPTER XXX.

Experiments with platinum and its compounds—Native metal—Purification by Deville's process—Platinic and platinous compounds—Döbereiner lamp—Tests—Rare metals: palladium, iridium, rhodium, ruthenium, and osmium	59
---	----

!

...

—

Contents.

vii

CHAPTER XXXVII.

	PAGE
Experiments with chromium and its compounds—Chromic acid—Properties of potassium—Chrome yellow—Chrome red—Chromic acid and anhydride—Reduction of—Chrome iron ore—Oxides and hydrates—Chlorides and oxychlorides—Chromic iron ore—Molybdenum, tungsten, and uranium	157

CHAPTER XXXVIII.

Experiments with iron and its compounds—Properties of iron— <i>Fer réduit</i> —Ferrous and ferric salts—Distinctive characters—Prussian blues—Hydrates and oxides—Dialysed iron—Scale preparations—Sulphides—Manufacture of iron from clay ironstone and hæmatite—Cast iron, wrought iron, and steel—Bessemer's process	172
---	-----

CHAPTER XXXIX.

Experiments with cobalt and nickel compounds—Meteoric iron—Alloys with iron—Ores, salts, oxides, &c.—Sympathetic ink—Cobalt <i>blue, green, and yellow</i> pigments—Nickel alloys—German silver, &c.—Extraction of metals from ores—Tests	206
---	-----

CHAPTER XL.

Experiments with aluminum compounds—Sources of oxide—Native forms of oxide—Sulphates—Alums—Uses of salts in dyeing—Chloride, extraction of metal from—Abyssinian gold—Ultramarine—Clays—Porcelain, earthenware, &c.—Rare elements related : gallium, cerium, lanthanum, didymium, erbium, terbium, yttrium, and scandium	222
--	-----

CHAPTER XLI.

Experiments with zinc and cadmium—Granulated zinc—Powdering the metal—Zinc oxide—Salts of—Extraction of metal from ores—Separation of cadmium—Oxide and salts of—Tests for zinc and cadmium	237
---	-----

CHAPTER XXXI.

	PAGE
Experiments with gold and its compounds—Gold washing and amalgamation—Gold coin—Auric and aurous compounds—Purple of Cassius—Gilding—Tests .	68

CHAPTER XXXII.

Experiments with silver and its compounds—Extraction, amalgamation, &c.—Silver coin—Nitrate (<i>Lunar caustic</i>) and other salts—Oxides—Argentous compounds—Uses of silver salts in photography—Tests .	75
---	----

CHAPTER XXXIII.

Experiments with mercury and its compounds—Extraction of mercury—Amalgams—Mercuric and mercurous compounds—Corrosive sublimate, calomel, &c.—Vermilion—Tests for mercury—Poisoning—Tests . . .	90
--	----

CHAPTER XXXIV.

Experiments with copper and its compounds—Ores—Alloys—Bronze coin—Cupric and cuprous compounds—Sulphides—Extraction of metal from—Tests for copper	110
--	-----

CHAPTER XXXV.

Experiments with lead and its compounds—Extraction from galena—Desilverising—Cupellation—Alloys of—Action of water on—Salts—Chrome yellow—White lead—Red lead—Oxides—Sulphides—Tests—Poisonous effects—Thallium	126
---	-----

CHAPTER XXXVI.

Experiments with manganese and its compounds—Pyrolusite and other oxides—Salts of—Manganates and permanganates—'Condy's fluid' as a disinfectant—Sulphide—Tests	144
---	-----

CHAPTER XXXVII.

	PAGE
Experiments with chromium and its compounds—Chromates of potassium—Chrome yellow—Chrome red—Chromic acid and anhydride—Reduction of—Chrome alum—Oxides and hydrates—Chlorides and oxychlorides—Chromic iron ore—Molybdenum, tungsten, and uranium	157

CHAPTER XXXVIII.

Experiments with iron and its compounds—Properties of metal— <i>Fer réduit</i> —Ferrous and ferric salts—Distinctive characters—Prussian blues—Hydrates and oxides—Dialysed iron—Scale preparations—Sulphides—Manufacture of iron from clay ironstone and hæmatite—Cast iron, wrought iron, and steel—Bessemer's process	172
--	-----

CHAPTER XXXIX.

Experiments with cobalt and nickel compounds—Meteoric alloy with iron—Ores, salts, oxides, &c.—Sympathetic ink—Cobalt <i>blue, green, and yellow</i> pigments—Nickel alloys—German silver, &c.—Extraction of metals from ores—Tests	206
---	-----

CHAPTER XL.

Experiments with aluminum compounds—Sources of oxide—Native forms of oxide—Sulphates—Alums—Uses of salts in dyeing—Chloride, extraction of metal from—Abyssinian gold—Ultramarine—Clays—Porcelain, earthenware, &c.—Rare elements related : gallium, cerium, lanthanum, didymium, erbium, terbium, yttrium, and scandium	222
--	-----

CHAPTER XLI.

Experiments with zinc and cadmium—Granulated zinc—Powdering the metal—Zinc oxide—Salts of—Extraction of metal from ores—Separation of cadmium—Oxide and salts of—Tests for zinc and cadmium	231
---	-----

CHAPTER XLII.

Experiments with magnesium compounds—Epsom salts— Magnesium carbonates—Oxides—‘Calcined magne- sia’—Chloride, extraction of metal from—Tests— Rare metal: beryllium or glucinum	PAGE 246
--	-------------

CHAPTER XLIII.

Experiments with calcium, strontium, barium—Calcium minerals—Limestone—Dolomite—Lime burning— Mortars and cements—Salts of metal—‘Plaster of Paris’—Tests—Strontium and barium compounds	252
---	-----

CHAPTER XLIV.

Experiments with lithium and potassium compounds— Lithium minerals—Carbonate—Phosphate—Tests— Potassium carbonate, extraction of metal from— Caustic potash—Potassium salts—Nitrate—Gun- powder—Tests	269
---	-----

CHAPTER XLV.

Experiments with sodium and ammonium compounds— Common salt—Direct conversion into ‘soda ash’ by ammonia process—Le Blanc’s process—Salt cake and soda ash—Carbonates—Caustic soda—Salts of metal —Tests—Rare elements: rubidium and cæsium— Ammonium salts	281
--	-----

APPENDIX.

Note on a classification of the elements.	294
Note on crystalline forms	297
Note on spectrum analysis	299
Analytical tables and instructions for systematic qualita- tive analysis	303

EXPERIMENTAL CHEMISTRY

FOR

JUNIOR STUDENTS.

PART III.

CHAPTER XXVI.

INTRODUCTION.

EXPERIMENTS WITH ARSENIC AND ITS COMPOUNDS.

THE group of pentad or five-link elements, to which nitrogen and phosphorus belong, includes, as already stated,¹ three other important members, namely, ARSENIC, ANTIMONY, and BISMUTH. Of these, the two former are in different degrees *pseudo-metallic* in character, and connect the great division of non-metals with that of metals, while bismuth more distinctly belongs to the latter class. The examination of these bodies therefore naturally precedes that of the elements usually classed as metals, and thus preserves the continuity of our line of study. Moreover, in experimenting with the metallic elements generally, the order followed will be found to nearly coincide with that of their atomicities and electro-

¹ Part II. page 270.

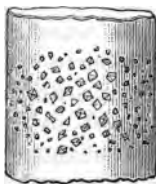
chemical relations, those of higher atomicity or electro-negative characters being first examined, wherever this course does not interfere with the natural grouping of the metals.

ARSENIC. *Symbol, As^v = 75. Weight of gaseous molecule = 300.*

We have already employed white oxide of arsenic (As_2O_3) in Experiment 106, and as this is the compound of the element that can be most easily procured, we shall use it in the following experiments, but the student must handle the body with great care, and preserve it and all of its derivatives under lock and key, as most arsenical compounds are well known to be deadly poisons.

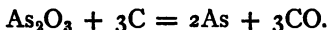
Experiment 350.—Introduce a small quantity of the powdered white oxide of arsenic into a *narrow* test-tube and gently heat. Note that the body is vaporised, without odour, and that small brilliant crystals, with triangular faces, as shown in fig. III, deposit on the cooler sides of the tube. These crystals have the same composition and properties as the original powder; hence the latter volatilizes unchanged.

FIG. III.



Experiment 351.—With a glass rod rub the crystals formed as above down the sides of the tube to the bottom; then place over the oxide some *dry* charcoal in rough powder, and apply heat to that part of the tube where the charcoal lies. Note that an odour resembling *garlic* is developed, and soon the

cool sides of the tube above the charcoal, as at *a*, fig. 112, become coated with a dark metallic-looking film, while above the latter some crystals of the oxide usually appear, unless air is excluded by nearly covering the mouth of the tube with the finger while heating. The dark metal-like body is the element ARSENIC, thus reduced from its oxide by means of carbon.



Arsenic as thus obtained has the metallic lustre, and is a moderately good conductor of heat and electricity. It is converted into vapour at $180^\circ \text{C}.$, and its specific gravity in that condition is 150 ($\text{H} = 1$); but, for reasons similar in kind to those already assigned in the case of phosphorus (vide Part II. page 269), the atomic weight of arsenic cannot be greater than 75; hence the gaseous molecule of the element, like that of phosphorus, includes *four* atoms. Moreover, the heat capacity of arsenic is such that 80.9 c.grs. contain at $100^\circ \text{C}.$ the same quantity of heat as 108 c.grs. of pure silver at the same temperature (see Part I. page 58); and this value is so close to 75, and so far removed from 150, that it amply confirms the lower atomic weight.

Elemental arsenic occurs in very small quantity in nature; it is chiefly prepared from arsenical pyrites, a native arsenio-sulphide of iron, FeSAs , termed *mispickel* by mineralogists. When this compound is strongly heated in vessels from which air is excluded,

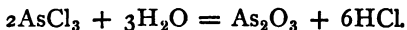
FIG. 112.



most of the arsenic sublimes, together with a little sulphur, and much of the crude 'metallic' arsenic of commerce is obtained by this method. It is commonly met with in the form of greyish-black lumps, and is used to a small extent as a poison for flies, but in much greater quantity in the manufacture of shot (see Lead).

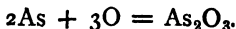
Experiment 352.—Powder a few grains of the dark grey elemental arsenic—which is very brittle—and allow it to fall into a jar of chlorine gas; note that the arsenic takes fire as it falls through the gas, and white fumes are produced, which can be condensed to an oily liquid. The latter has the composition indicated by the formula AsCl_3 , and results from the direct union of the two elements. This trichloride is the only compound of chlorine and arsenic yet known; the arsenic analogue of PCl_5 is therefore wanting.

When water is added to the contents of the jar the trichloride is decomposed thus:—



Tri-iodide and tribromide of arsenic are known, and decompose with water like the trichloride.

Experiment 353.—Heat a minute fragment of the elemental arsenic on the bottom of a wide test-tube; note that the element disappears and crystals of the oxide are deposited on the side of the tube.

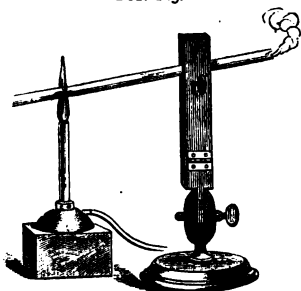


Thus arsenic is easily oxidised when heated in air.

Experiment 354.—Obtain a small quantity of

native *mispickel*¹—FeSAs—roughly powder it, and introduce a small quantity into a glass tube, open at both ends (see fig. 113). This tube should be about 30 c.ms. long and 5 to 7 m.ms. in diameter. The powdered mineral is deposited in the tube about 4 or 5 c.ms. from one end, and the glass on which the mineral rests is gently heated in the gas flame, as shown in the figure.

FIG. 113.



It is necessary to incline the tube so that the unheated end shall be well above that which is in the gas flame; thus a current of air is established over the heated mineral, and oxidation of its constituents proceeds. Sulphur dioxide gas (SO_2) issues from the top of the tube, and more or less of a nearly white or yellowish sublimate is observed in the tube above the ore, and throughout this the easily recognised crystals of As_2O_3 can be detected, while the residue assumes a very dark brown colour, especially when allowed to cool; this is due to the conversion of the iron into Fe_2O_3 . The complete decomposition of the mineral is represented by the equation—



This mode of decomposing an ore is termed

¹ Instead of this ore the mineral *leucopyrite*, FeAs_2 , a simple arsenide of iron, may be employed.

roasting, and the process just carried out is one of the best illustrations of this very common treatment of metallic ores.

On the large scale the glass tube is replaced by a long iron tube, or a brick furnace, in which mispickel, or other ore containing arsenic, is roasted, and the fumes are passed through long condensing chambers in which the impure oxide of arsenic is deposited. This crude material is purified by resublimation in iron pots, and then appears as the 'white arsenic,' or simply, though incorrectly, 'arsenic' of commerce.

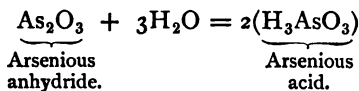
This body is a deadly poison, and when sold as a white powder has been frequently mistaken for many innocuous white bodies. Thus it has been added to flour instead of 'bread soda,' to soup instead of salt, &c., and has caused so many fatal accidents that the Sale of Poisons Act now requires the vendors to colour it with a small proportion of either soot or indigo.

The sesquioxide of arsenic is met with in commerce in two forms; one of these is a white crystalline powder, the other is a glassy mass; the latter gradually undergoes change into the former, and becomes opaque.

Experiment 355.—Digest with gentle heat a small quantity of crystalline As_2O_3 with some water in a test-tube. Note that the solid seems to be insoluble in water. Allow the powder to subside and pour off most of the liquid into a clean test-tube; ¹ note that

¹ Although the specific gravity of the oxide is greater than that of water (3.7), some of the powder persistently floats on the latter, owing to adhesion of air which buoys up the particles. This is a point of some medico-legal interest.

the solution is sensibly *acid* to blue litmus paper. Add to the liquid a few drops of solution of ammonia-silver nitrate,¹ a canary-yellow precipitate is obtained which has been found to consist of $\text{Ag}'_3\text{AsO}_3$, evidently the silver salt of the acid H_3AsO_3 . We conclude, then, that arsenic sesquioxide is sensibly soluble in water (one part dissolves in forty parts if the mixture be boiled for an hour and allowed to cool, but if boiled for a few minutes only, about eighty parts of water are required for the solution of one of the oxide), and acts as the anhydride of the tribasic acid, whose formula is given above, which is termed *arsenious acid*.



When the solution of the acid is evaporated the anhydride separates out ; hence the acid is easily decomposed—so easily that it has not been isolated in a pure state.

Experiment 356.—Add to some of the solution of arsenious acid prepared in the last experiment a few drops of ammonia-copper sulphate. Note that a grass-green precipitate is formed. The composition of this is represented by the formula $\text{Cu}''\text{H}'\text{AsO}_3$ —an arsenite of copper and hydrogen commonly known as *Scheele's Green*.² This compound is often, and

¹ Prepared by adding to silver nitrate very dilute ammonia drop by drop, with agitation, until the precipitate first formed is *just* redissolved. The copper compound is prepared in the same way from copper sulphate solution.

² Another pigment, termed *Schweinfurt Green*, is obtained by boiling equal parts of arsenic sesquioxide and copper acetate with water for some hours.

improperly, used as a pigment for wall-papers, and many cases of chronic arsenical poisoning have arisen in consequence, for the pigment, though not volatile, is easily detached from the paper and mechanically carried through the air of a room to the lungs and skins of the inhabitants. In order to test a piece of such paper for arsenic, dry the material well, scrape off some of the green pigment, introduce it into a narrow tube of hard glass and cover with a layer of powdered charcoal. Heat as in Experiment 351, when a dark ring of arsenic will be obtained, or crystals of the oxide on the cooler portions of the tube, if the pigment be arsenical.

Experiment 357.—Dissolve a small quantity of potassium carbonate, K_2CO_3 , in half a test-tube of water and add a little arsenic sesquioxide : on boiling the liquid, solution of the arsenic takes place. At first solution is not accompanied by evolution of carbon dioxide gas, but if the boiling be long continued gas is evolved and a true potassium arsenite— K_3AsO_3 —is formed. When this solution contains *four grains* of the oxide and the same weight of potassium carbonate in one fluid ounce of water, coloured red with compound tincture of lavender, it constitutes *Fowler's solution* or *Liquor arsenicalis*, B. P. For the action of free iodine on this solution see Experiment 363. The oxide is readily soluble in the caustic alkalies KOH and NaOH, and at once forms arsenites.

Experiment 358.—Boil some arsenic sesquioxide with water containing a few drops of hydrochloric acid. Solution is easily effected, and if the liquid contains much arsenic when hot it will deposit crystals of the

anhydride on cooling. A solution containing four grains of the oxide in one ounce of dilute hydrochloric acid constitutes the *Hydrochloric solution of arsenic*, B. P. This liquid does not contain arsenic trichloride— AsCl_3 —as the latter is easily decomposed by water in the manner already pointed out under Experiment 352, though during solution a little of the trichloride is formed and volatilised from the boiling liquid.

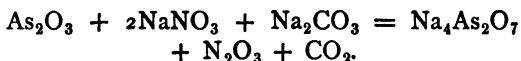
Experiment 359.—We have already learned from Experiment 106 that As_2O_3 is oxidised by moderately strong nitric acid, and a new acid of arsenic obtained containing an atom of oxygen more than arsenious acid, and termed *Arsenic acid*— H_3AsO_4 . Repeat the experiment in a test-tube, and boil off as much of the excess of nitric acid as possible; then dilute some of the solution with water and add a few drops of ammonia-silver nitrate. Note that a dull *brick-red* precipitate is formed whose composition is represented by the formula Ag_3AsO_4 or silver arsenate. Arsenious and arsenic acids are therefore easily distinguished by the colours of their silver salts (see Experiment 355).

Experiment 360.—Take some of the arsenic acid solution and evaporate it rapidly to dryness in a capsule; a white deliquescent mass is left which consists of arsenic anhydride— As_2O_3 —and this, when dissolved in water, reproduces arsenic acid, as shown by the action on litmus and by the silver test.

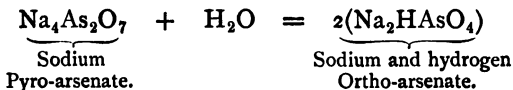
Experiment 361.—To another portion of arsenic acid solution add sodium carbonate until effervescence ceases, then evaporate until crystals form. These crystals consist of Na_2HAsO_4 , $12\text{H}_2\text{O}$, and therefore

correspond in composition with the common sodium phosphate (Part II. page 259). Moreover, the crystals are almost identical in form with those of the phosphate; hence the two salts are said to be *isomorphous*.¹ The British Pharmacopœia directs this salt to be prepared by the following indirect process.

Experiment 362.—Heat in a tube a mixture of about equal weights of arsenic sesquioxide and sodium nitrate with half the weight of dry sodium carbonate. The mixture fuses and begins to effervesce; continue the heat until gas ceases to come off, then allow the residue, which consists of sodium pyro-arsenate— $\text{Na}_4\text{As}_2\text{O}_7$ —to cool and solidify. The following change takes place during fusion :—



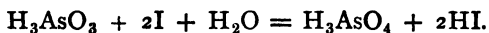
The residue is boiled with water, in which the sodium pyro-arsenate dissolves; at the same time it unites with a molecule of water and forms the sodium and hydrogen ortho-arsenate prepared in the last experiment; the latter can be crystallised out from the solution.



The crystallised salt contains twelve molecules of water of crystallisation, five of which are lost on mere exposure to dry air, and the remaining seven molecules of water are expelled on heating the body to 150° C.

¹ See page 12.

Experiment 363.—Add solution of iodine in potassium iodide drop by drop to some of the solution obtained in Experiment 357. Note that the colour of the iodine disappears until a point is reached at which no further decolouration occurs. If the solution be examined it is now found to contain arsenic acid, or rather its sodium salt, the iodine having served as an indirect oxidising agent. Thus, assuming the acids to be free—



This is the foundation of process for the volumetric estimation of arsenic in the arsenious condition. For this purpose it is necessary to have a considerable excess of solution of sodium hydrogen carbonate¹— NaHCO_3 —present, in order that the arsenic and hydriodic acids produced may be neutralised as fast as they are formed. The reaction is irregular and incomplete unless this precaution is adopted.

Experiment 364.—Dilute a few drops of arsenic acid solution, and add some magnesium sulphate solution followed by ammonium hydrate, as in Experiment 345 with a phosphate, a crystalline precipitate forms, which contains $\text{Mg}''\text{NH}_4'\text{AsO}_4, 6\text{H}_2\text{O}$. This compound is isomorphous with the corresponding phosphate, and affords magnesium pyro-arsenate— $\text{Mg}_2\text{As}_2\text{O}_7$ —when heated to low redness. Generally the arsenates and phosphates closely correspond in crystalline form and chemical constitution, and the analogies can be traced not only through the

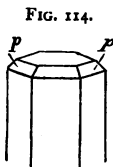
¹ The neutral carbonate Na_2CO_3 cannot be used for this purpose, as it decolourises a very sensible quantity of iodine, even in the absence of arsenic.

ortho-derivatives, but through pyro- and meta-compounds, for meta-arsenates have been obtained, though these bodies, unlike the meta-phosphates, are not known in solution. Analogy would lead us to conclude that arsenic is a pentad like phosphorus, and the constitution of arsenates can best be represented on this view, but in most of the common compounds of the element, *e.g.* the trichloride, arsenious anhydride, &c., it acts as an apparent triad.

Experiment 365.—Add a few drops of lead nitrate solution to a liquid containing some alkaline arsenate. Note that a white precipitate is formed as in the analogous case of a phosphate. The composition of the body precipitated is represented by the formula $\text{Pb}''_3(\text{AsO}_4)'''_2$; it therefore corresponds to lead ortho-phosphate, $\text{Pb}''_3(\text{PO}_4)'''_2$, which is formed under similar conditions.

Isomorphism.—Lead arsenate and phosphate both occur in nature in combination with lead chloride as well crystallised minerals; the mineralogical name of the arsenate is *mimetesite*, and of the phosphate

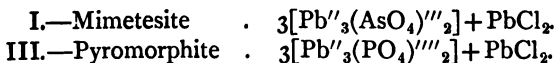
pyromorphite. When well-defined natural crystals of the two minerals are examined, they are found to be very similar in form—that is to say, they are six-sided prisms resembling fig. 114, whose base is a regular hexagon, more or less modified by the planes *p p* derived from a six-sided pyramid.



Crystals differing but little from the above type, and from each other in form, have been found to vary in composition to the very wide extent shown by the following analyses:—

	I.	II.	III.
Arsenate of Lead .	90.07	71.70	—
Phosphate of Lead .	—	19.00	89.91
Chloride of Lead .	9.93	9.30	10.09
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

The formulæ derivable in the usual way from analyses I. and III. are



Hence these bodies are strictly analogous in chemical constitution as well as almost identical in crystalline form. So close is this relationship that, as in Analysis II. above, a portion of the arsenate of lead can be replaced by the phosphate without any change of structure, *but such a replacement always takes place in equivalent, or rather molecular, proportions.* Thus, in the above instances the molecular weights of lead arsenate and phosphate are respectively 899 and 813, and it is in the ratio of these weights that the compounds replace each other in the crystalline group.

Facts of the order just indicated led Mitscherlich in 1819 to enunciate the general principle that *analogous groups of elements can replace each other in composition without essential alteration of crystalline form*; but it must be remembered that any such replacement takes place in the proportions already pointed out.

Mitscherlich's 'law of isomorphism' is often used in chemistry to determine the class relationships of particular elements, and incidentally to settle questions

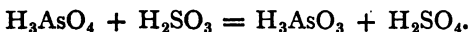
affecting atomicity, &c. In this way, as we have seen, the natural affinities of arsenic and phosphorus can be traced; and we shall presently refer to the rare element vanadium, which can be similarly connected with the phosphorus and arsenic group; while later on, in the cases of iron and aluminium and other metals, the law will be found to prove a valuable aid in solving problems which are otherwise difficult of solution.

An intelligent student will scarcely fail to recognise in the facts on which the law of isomorphism rests so many apparent contradictions to the 'law of constant composition,' which he has been rightly taught to regard as the foundation of the science of chemistry. The apparent conflict between these two great principles admits of a satisfactory explanation, if we suppose (and we have good reason to do so) that the *crystalline* molecule is a much more complex system than the *chemical* molecule, and is made up of a large number of the latter. Thus the chemical molecule of mimesite may be represented by the formula above given, whereas a crystal of the mineral is probably built up of many such groups, arranged symmetrically about the crystalline axes, just as bricks build up a pillar. It is very easy to understand, then, that during the growth of such a crystal in a liquid containing not only arsenate but the phosphate of lead, some of the chemical molecules of the latter may seize the opportunity afforded to them of entering as chemical units into the formation of a structure similar to that which they could produce unaided, and the crystal, when complete, would necessarily exhibit the mixed

character of the mineral of the second analysis, because some of the bricks (*i.e.* chemical molecules) consist of arsenate and others of phosphate of lead. The substitution necessarily takes place in the ratio of the molecular weights of the bodies concerned.

Having sufficiently traced the products of oxidation of arsenic, we shall now examine the effect of reducing agents on arsenic acid and other compounds.

Experiment 366.—Add some sulphurous acid solution to arsenic acid contained in a test-tube, and boil until all smell of the former body completely disappears. Now test the residual liquid with ammonia-silver nitrate, and note that yellow silver *arsenite* is formed; therefore sulphurous acid reduces arsenic acid¹ to arsenious; thus—



Sulphurous acid is unable to carry the reduction further; but we already know from Experiment 114 that nascent hydrogen is a reducing agent of great power, hence we shall try its effect on arsenious acid.

Experiment 367.—Fit up the hydrogen evolution bottle as shown in fig. 115, and have the bent tube *t* drawn out to a fine jet.² Introduce some *pure* zinc and water into the bottle, then pour in a little *pure* sulphuric acid. If the materials are pure, gas will be slowly evolved, but the addition of a few drops of copper sulphate will lead to brisk evolution of gas, owing to electro-chemical action. When air has been

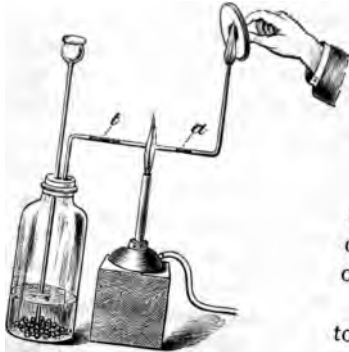
¹ See further experiment 375.

² This should be narrow, and made of glass which is free from lead and difficult of fusion, or 'hard.'

Experimental Chemistry.

expelled from the bottle, and the test recommended in Experiment 20 applied, kindle the gas at the jet and note that the burning hydrogen, if the materials employed are pure, does not cause any stain on a piece of white porcelain when the latter is depressed in the flame. Now pour in through the funnel tube a few drops of solution of arsenious acid; presently the flame changes to a pale bluish colour, and when

FIG. 115.



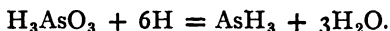
allowed to impinge on the white porcelain a dark stain is left on the latter. The dark substance deposited from the flame is arsenic and is easily identified, as it is very soluble in a solution of 'bleaching lime' or other hypochlorite.¹

Apply a gas flame to the part of the tube marked *a*, and note that a mirror-like deposit forms just beyond the heated portion. This can also be shown to be arsenic when the tube is removed and washed with the bleaching lime solution. Before doing so, however, remove the flame from *a*, turn the point of the jet downwards, and make the issuing gas bubble through solution of silver nitrate contained in a test-tube. Note that a dark

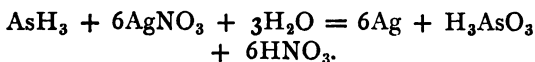
¹ The solution of the stain is due to the oxidation of the arsenic to arsenious acid or an arsenite.

precipitate forms in the solution, and this can easily be shown to consist of finely divided *metallic silver*.

It is evident that arsenic is given off from the evolution apparatus in some gaseous form, and the particular form is that of an arsenide of hydrogen, whose formula is AsH_3 . This body is the result of the complete deoxidation of arsenious acid by nascent hydrogen, thus—



This hydride is easily decomposed by heat into hydrogen and arsenic, as in the heated tube and in the flame. Moreover, as we have seen, it acts as a reducing agent for silver nitrate, and this action is explained by the following equation—



The action of nascent hydrogen generated as above serves as a most convenient and delicate *test* for arsenic, as the effects of heat and of silver nitrate on the arsenical gas are quite characteristic; this mode of recognising the element is termed *Marsh's test*.¹

The hydride of arsenic obtained in this experiment, mixed with hydrogen, is when pure a colourless and highly poisonous gas, which the operator must be careful to avoid inhaling. It is evidently analogous in composition to phosphuretted hydrogen PH_3 and ammonia NH_3 , though it does not possess the spon-

¹ In applying this test to the search for minute quantities of arsenic it is necessary to bear in mind that the zinc and acid employed may contain traces of arsenic; hence the materials should all be carefully tested in the first instance.

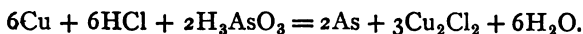
taneous inflammability of the former or the alkaline characters of the latter. A solid hydride is known whose formula is As_2H or As_4H_2 .

Experiment 368.—We already know (from Experiment 114) that zinc and strong sodium or potassium hydrate solution when boiled together afford hydrogen. Repeat this experiment, adding a few drops of arsenious acid to the contents of the tube, and cover the mouth of the latter with a piece of bibulous paper moistened with silver nitrate solution. The paper is soon discoloured owing to the action of the AsH_3 evolved on the silver salt, as already explained. This mode of testing for arsenic is termed *Fleitmann's test*.

In the above two instances of reduction of arsenious acid by nascent hydrogen we do not obtain the free element but its hydride, and this occurs when many other as highly electro-positive metals as zinc are used for the reduction; we shall therefore next try the metal copper, which is electro-negative to zinc though electro-positive to arsenic.

Experiment 369.—Introduce into a test-tube a few bright copper turnings, cover them with water and add a few drops of strong hydrochloric acid; no gas is evolved even when the mixture is gently warmed. Now add a few drops of solution of arsenious acid and boil for a minute, the copper quickly acquires a grey metal-like coating; pour off the acid liquid and wash the coated copper repeatedly with pure water, then shake the turnings out on a piece of filtering paper, and dry the copper by pressure between the folds of paper. On examination the coating is seen to resemble arsenic in appearance. Next introduce

the turnings into a narrow hard glass tube closed at one end and heat; note that the copper regains its colour and a sublimate is obtained which is of a grey mirror-like character, if the tube be very narrow and air excluded, or crystalline and recognisable as arsenic sesquioxide if the tube be moderately wide. In the first part of the experiment, then, the copper displaces the arsenic from solution, and the latter separates as a coating on the undissolved copper, thus—

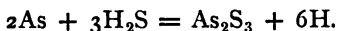


The cuprous chloride, Cu_2Cl_2 , remains in solution. When the copper coated with arsenic is heated the latter volatilises and condenses as the free element or the oxide, according to the proportion of air or oxygen the vapour meets in the tube. This mode of detecting arsenic is termed *Reinsch's test*, and is of great value in separating the poison from complex mixtures.

Having now examined the chief oxides of arsenic and their acids, and again obtained the element by the copper reduction process just carried out, we shall make a new departure and attempt the formation of a sulphide of arsenic.

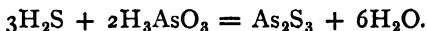
Experiment 370.—Take the hard glass tube containing an arsenical film obtained in Experiment 367, and connect it with an apparatus evolving sulphuretted hydrogen (Experiment 276) and gently heat the part of the tube at which the film lies while a current of H_2S passes. Note that the colour of the arsenical layer changes and a yellow body is formed, which partially

sublimes. This yellow substance is arsenic sesquisulphide, thus formed—



When the tube is removed, water introduced and the sublimate digested with it, solution does not take place, nor is the body dissolved if a little hydrochloric acid be added. The insolubility of the sulphide in water leads to the conclusion (which is in accordance with Berthollet's first law, Part I. appendix) that it can be obtained from solution of arsenious acid.

Experiment 371.—Pass a current of sulphuretted hydrogen gas through arsenious acid solution containing a *little free hydrochloric acid*. A bright yellow precipitate quickly forms, which consists of the sesquisulphide—



This precipitate does not dissolve in moderately strong hydrochloric acid, but it is easily soluble in *ammonium hydrate*, and is reprecipitated when the liquid is neutralised by hydrochloric acid. The sulphide of arsenic obtained in the experiment is identical in composition with the native sulphide termed *Orpiment*. Another native sulphide is known whose empirical formula is AsS . The mineralogical name of this body is *Realgar*; it is of an orange red colour, and often occurs in nearly transparent crystals, whereas orpiment is yellow and usually almost opaque.

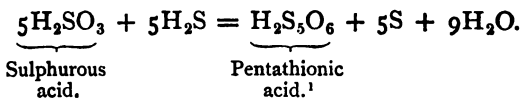
Experiment 372.—Prepare some of the arsenic sesquisulphide as in the last experiment, wash it by decantation or on a filter, in order to free it from acid, and then pour over it some of the ammonium sulphy-

drate solution prepared in Experiment 286. The arsenic compound dissolves and forms a slightly yellowish liquid, which has been found to contain the compound $(\text{NH}_4)_3\text{AsS}_3$, when the sulphhydrate has been used in considerable excess. This body is evidently the sulphur analogue of an arsenite, and is termed *ammonium sulpharsenite*. The solution of the latter is easily decomposed by free hydrochloric or other acid, As_2S_3 separating.

Experiment 373.—Divide in two parts solution of arsenic acid, H_3AsO_4 , to which a few drops of hydrochloric acid have been added. Through one pass a current of sulphuretted hydrogen, and apply heat. Note that a slight yellow precipitate very slowly forms, and this is found to consist chiefly of a mixture of As_2S_3 and sulphur.

Experiment 374.—Add to the second portion a few drops of sulphurous acid, boil off the excess, and pass sulphuretted hydrogen. The usual yellow precipitate of As_2S_3 forms immediately. In this case the rapid action is due to the reduction of arsenic acid to arsenious by the sulphurous acid (see Experiment 366). The results of the comparison just made indicate the necessity for adding a reducing agent, such as sulphurous acid, to a liquid in which arsenic is to be tested for by means of sulphuretted hydrogen, especially if there is any reason to suppose that the element is present in the form of arsenic acid; but any considerable excess of sulphurous acid must be boiled off before passing H_2S , as the latter reacts with H_2SO_3 , and much sulphur is deposited, which latter may mislead the analyst. The separation of

sulphur in such a case is due to the following reaction :—



Experiment 375.—Although As_2S_5 is not formed by the action of sulphuretted hydrogen on arsenic acid, the body is easily prepared by fusing 246 c.grs. of As_2S_3 with 64 c.grs. of S ; the higher sulphide corresponding to As_2O_5 is then formed, and is soluble in the alkaline sulphhydrates, forming *sulpharsenates*, which are analogues of the arsenates already referred to. These compounds are not as yet of sufficient importance to warrant more detailed examination in a junior course.

The tests for arsenic described in the preceding pages are the *silver test*, *copper or Scheele's test*, *reduction*, *Marsh's*, *Reinsch's*, and *sulphuretted hydrogen tests*.

Poisonous action.—Arsenic sesquioxide, or arsenious anhydride, is a powerful irritant poison, and has caused death in doses of 20 c.grs. (3 grains). The earlier symptoms are nausea, vomiting, abdominal pain, cramp—chiefly in the legs—followed by collapse and death. In some cases the symptoms have been mistaken for those of cholera. When given in small and repeated doses gastric irritation occurs, the eyes are suffused, the eyelids red and inflamed, the hair gradually falls, and eruptions on the skin often follow, these symptoms being commonly accompanied by general depression. Even minute medi-

¹ See Part II., under Experiment 314.

cinal doses, when long continued, give rise to some of these symptoms.

Antidote.—The best chemical antidote is moist and recently precipitated ferric hydrate; this can be roughly and rapidly prepared by adding sodium or ammonium hydrate in *slight excess* to the *tincture of perchloride of iron*, B.P., after diluting the latter with twice its volume of warm water. A bulky brown precipitate forms, which is caught when the mixture is thrown on a cloth, where it is quickly washed by pouring some fresh water over the precipitate; the latter is then squeezed in the cloth, and can be at once administered. A teaspoonful may be given at short intervals until five or six are taken. The theory of the action of this antidote is stated under ferric hydrate (see Iron).

Detection of arsenic in cases of poisoning.—In the cases of fluids containing particles of food as well as dissolved organic matters, it is difficult to obtain satisfactory evidence of the presence of arsenic without previous treatment. This consists in digesting the organic mixture at a gentle heat, with the addition of about *one-sixth*¹ of strong hydrochloric acid; then filter through fine muslin which has been previously cleansed by frequent washing in boiling water. Introduce *half* the filtered liquid into a flask, and suspend a bunch of clean copper turnings in the liquid by means of a thin copper wire. Then boil gently for half an hour, remove and wash the

¹ This large proportion is necessary in case any of the poison happens to be in the condition of arsenic acid, as the latter is reduced by the copper only in presence of a large excess of the acid.

copper thoroughly, and dry it between folds of bibulous paper. Whether arsenic is present or not, the copper usually becomes grey ; hence it must be treated as in Experiment 369, and a sublimate of arsenic or its oxide obtained from it before the conclusion can be drawn that the poison is present.

The second portion of the liquid is to be introduced in small quantities into an apparatus such as that used in Marsh's test (Experiment 367), and a deposit of arsenic obtained in the tube and on porcelain ; the deposits are then identified as already described. In the application of all these tests it is necessary to make a rigorous examination of all the materials used for traces of arsenic, as the copper, zinc, and acids used frequently contain traces of the poisonous element.

The method of *dialysis*, or diffusion through an animal membrane, has been employed in the separation of arsenic from organic mixtures ; but the methods above given are of chief practical value.

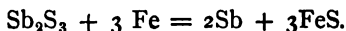
CHAPTER XXVII.

EXPERIMENTS WITH ANTIMONY AND ITS COMPOUNDS.

ANTIMONY— $\text{Sb}^v = 122$. The most easily obtained compound of this element is a native sulphide termed *black antimony*, whose composition is Sb_2S_3 . This mineral is usually found in tolerably pure condition, and even when impure, owing to the presence of earthy substances, it can be easily separated from the latter by simple fusion, as the sulphide becomes liquid below a red heat, and separates from the impurities, which are much less fusible. In this way much of the commercial sulphide is separated from the crude ore.

Experiment 376.—Powder some of the brittle antimony sulphide just referred to, and mix it with about half its weight of very small iron tacks; introduce the mixture into a common clay crucible, and cover the mixture with a layer of dried sodium carbonate. Now place the crucible in an ordinary fire, and gradually raise the vessel and its contents to a full red heat, and keep it at this temperature for ten minutes or more; then remove the crucible from the fire and allow it to cool. If the process has been properly conducted, a metallic button can be extracted, when the crucible is broken; this has evidently formed under a layer of material technically termed 'slag,' resembling the

ferrous sulphide formed in Experiment 273 by the direct union of iron and sulphur. In this case—



The button consists of antimony displaced from its sulphide by the more electro-positive iron.

Much of the commercial antimony is obtained by a similar process.

Clean the adherent impurities from the piece or pieces of antimony, and examine the element. Note that it breaks readily into fragments under a blow of a hammer, or in a mortar; it is therefore *brittle*, and the bright surfaces exhibit a fine metallic lustre, while the colour is nearly as white as that of silver. Its specific gravity is 6·8 (water = 1). It conducts electricity and heat well, and is easily fused in a test-tube at a temperature below a red heat (428° C.). When strongly heated in the air it readily oxidises, and becomes coated with a white incrustation, but it does not easily tarnish at ordinary temperatures. The characters of pure antimony are apparently those of a *metal*, but we have yet to learn whether it is capable of taking the place of hydrogen or electro-positive radicle in an acid and forming salts.

The weight of metallic antimony that contains at 100° C. the same quantity of heat as 108 c.grs. of metallic silver at the same temperature is 129·7 c.grs.

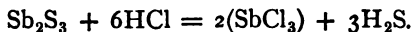
Metallic antimony is chiefly employed in the arts, in the manufacture of certain metallic mixtures, or ‘alloys,’¹ as those composite metals are termed—such

¹ *Amalgams* are alloys of mercury with other metals. True

as *type-metal*, which consists of two parts lead and one each of tin and antimony, and Britannia metal, an alloy of tin with about one-sixth of antimony. In these cases the antimony gives hardness to the alloy, and enables it to resist wear and tear, and communicates to type-metal the very important property of expanding at the moment of solidification, so that a sharp impression is obtained of the mould in which the letter or figure is cast.

The most convenient source of antimonial compounds is the native sulphide we have already used in the preparation of the metal.

Experiment 377.—Boil a small quantity of the grey sulphide of antimony in a test-tube with strong hydrochloric acid ; note that the smell of sulphuretted hydrogen is developed while the mineral dissolves. As already pointed out, under Experiment 276, this is the best mode of preparing sulphuretted hydrogen in a pure condition. The following equation expresses the change :—



When gas ceases to be evolved, allow the residue to stand in order that insoluble matter may deposit, then pour off the clear liquid into a clean test-tube. This solution now contains the antimony trichloride formed in the above reaction. This liquid forms the common *Butter of antimony*¹ of the druggist, and the

alloys possess the general metallic characteristics ; in some instances alloys seem to contain feeble chemical compounds of two or more metals.

¹ Often used as a powerful caustic by veterinary surgeons.

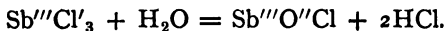
Solution of chloride of antimony of the British Pharmacopœia. The liquid should be nearly colourless, but is usually reddish-brown, owing to the presence of iron derived from the impure antimonial ore.

Experiment 378.—Place some of the liquid in a small retort, or a tube bent in the shape of a retort, and distil nearly to dryness ; a yellowish buttery mass condenses in the neck of the vessel at the end of the process ; this is the antimony trichloride in a nearly pure condition. When this chloride is liquefied, by gently heating in a tube, and a current of chlorine gas passed through it, the gas is absorbed, and a colourless fuming body is obtained, which does not solidify on cooling. This is a higher chloride— SbCl_5 —antimony pentachloride, which is identical with a body formed along with the trichloride when powdered antimony undergoes spontaneous combustion in a large excess of chlorine, as in Experiment 144. In the lower chloride the antimony atom evidently acts as an apparent *triad*, and in the higher chloride as a *pentad*.

Experiment 379.—Pour some of the solution of antimony trichloride obtained in Experiment 377 into about twenty times its volume of distilled water. Note that a white precipitate immediately forms, and if the turbid mixture be allowed to stand after thorough mixture, the white body subsides. The latter, when produced under the conditions given, is found on analysis to have the composition represented by the formula $\text{Sb}''' \text{O}'' \text{Cl}'$;¹ it is therefore an oxychloride of

¹ *Termed in the older books Powder of Algaroth.*

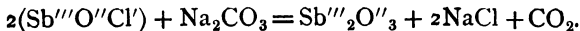
antimony, resulting from the decomposition of the trichloride by a molecule of water—



The oxychloride is easily redissolved by the addition to any liquid in which it is formed of a few drops of *strong* hydrochloric acid. The latter reproduces the soluble trichloride.

As the antimony trichloride parts readily with some of its chlorine on mere mixture with water, it should be possible to eliminate the last atom from the oxychloride. To test this point, make—

Experiment 380.—Pour off the water from the precipitated oxychloride of antimony formed in the last experiment, and pour over the moist compound solution of sodium carbonate; effervescence takes place, indicating that chemical action has occurred, and the gas evolved can be easily identified as carbon dioxide, while the precipitate, though apparently unchanged, when collected on a filter, washed with water, and dried at a temperature of 120°C. , is found on analysis to consist of the antimony sesquioxide Sb_2O_3 ; thus all the chlorine is eliminated by the alkali. This change is easily explained by the equation—



The convenient method just followed for the elimination of the chlorine of the oxychloride is that directed by the British Pharmacopœia for the preparation of the oxide. A mixture of one part of the latter and two of pure calcium phosphate forms the

Antimonial powder B.P.—the representative of the well-known patent medicine *James's Powder*.

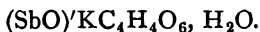
The sesquioxide of antimony is easily soluble in strong hydrochloric acid, and reproduces the trichloride.

Antimony sesquioxide is evidently analogous in composition to arsenic, phosphorus and nitrogen sesquioxides, but, unlike those bodies, does not dissolve in water to any appreciable extent, and does not directly form an acid with the elements of water. Boiling caustic soda, however, dissolves the oxide, and the solution deposits on cooling small crystals, of a body whose composition is represented by the formula $\text{NaSbO}_2, 3\text{H}_2\text{O}$. This compound may be regarded as the sodium salt of an antimonious acid, HSbO_2 , whose anhydride is the oxide Sb_2O_3 ; but the latter so easily forms the chloride by solution in hydrochloric acid, that there is some ground for the suspicion that the element can take also the place of basic hydrogen in other acids. Hence we make—

Experiment 381.—Gently heat in a test-tube a small quantity of the oxide, Sb_2O_3 , with about two c.cs of strong sulphuric acid. Note that the oxide dissolves, and in cooling the acid liquid a crystalline compound separates, which has been found to consist of antimony sulphate, $\text{Sb}'''_2(\text{SO}_4)'''_3$. This is a true salt in which the two atoms of triad antimony are electro-positive to the acidic group.

Antimony is thus the first of the family of pentad elements that not only presents the physical characters of a metal, but also that can occupy the basic or *electro-positive* position in a salt.

Experiment 382.—Digest at a gentle heat three grams of Sb_2O_3 and four grams of acid tartrate of potassium, commonly called 'cream of tartar'— $\text{HKC}_4\text{H}_4\text{O}_6$ —with about twenty-five cubic c.ms of water. Solution slowly takes place, and when nearly complete, the liquid is filtered while hot. On cooling crystals separate and can be collected, drained, and air dried on bibulous paper. The compound thus obtained is the well-known *tartar emetic*. The empirical formula of this body is $\text{SbKC}_4\text{H}_4\text{O}_7, \text{H}_2\text{O}$, but if we exclude the molecule of water and compare the formula with that of the 'cream of tartar,' we see at once that the latter has lost an atom of hydrogen, and gained the group SbO , or stibonyl. Now, if antimony be a triad this group should act as a monad compound radicle ($\text{Sb}''' \text{O}''$), and be capable of taking the place of one atom of monad hydrogen. On this view the rational formula for tartar emetic is written—



This compound is easily soluble in hot and cold water, and the solution may be diluted without causing turbidity, unlike the solution of the trichloride. When the solid salt is heated with strong sulphuric acid it becomes black, and a smell of burnt sugar is developed owing to the decomposition of the organic acid radicle.

Add a few drops of hydrochloric acid to a solution of tartar emetic, a white precipitate of $\text{Sb}''' \text{O}'' \text{Cl}'$ is formed, which easily dissolves in excess of acid and forms solution of trichloride. The precipitate is not formed if tartaric acid be previously added.

Experiment 383.—Pour some nitric acid over a small quantity of Sb_2O_3 contained in a porcelain crucible, mix well and evaporate off the acid, then gently heat the dry residue for a few minutes; the residue is a yellowish powder, and, when a portion is heated with hydrochloric acid, it dissolves very slowly, unlike the sesquioxide which rapidly passes into solution. The residue is, in fact, pentoxide of antimony, Sb_2O_5 , obtained as above by the action of nitric acid.¹ The compound is very slightly soluble in water, to which, however, it communicates a faint acid reaction. The inference is that it is the anhydride of an acid, and therefore the analogue of nitrogen, phosphorus, and arsenic pentoxides. The anhydride dissolves in potassium hydrate and the solution is found to contain a potassium antimonate, KSbO_3 , which is the analogue of potassium nitrate and metaphosphate.

An acid potassium salt of another antimonie acid is known, whose formula— $\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7$,²—indicates that the acid from which it is derived— $\text{H}_4\text{Sb}_2\text{O}_7$ —is the analogue of pyrophosphoric acid— $\text{H}_4\text{P}_2\text{O}_7$.

Experiment 384.—Heat to full redness the small quantity of the pentoxide left in the crucible in the last experiment. Note that it becomes nearly white when cold, and resembles in appearance the sesquioxide originally employed; but, unlike it, does not easily dissolve in hydrochloric acid. This body is a

¹ This body is also formed when antimony, or one of its alloys, is digested with nitric acid.

² This is sometimes used as a test for sodium, with which it forms a slightly soluble compound.

new oxide, whose formula is SbO_2 or Sb_2O_4 ; ¹ it is chiefly interesting because it is the form in which antimony is almost invariably weighed in quantitative analysis, and is, as we have seen, easily obtained from either the sesqui- or pentoxide.

Experiment 385.—Add hydrochloric acid, drop by drop, to solution of tartar emetic until the precipitate of SbOCl first formed is redissolved (see Experiment 382); then add sulphuretted hydrogen water until the liquid smells strongly of the gas. Note that a fine orange-coloured precipitate forms. This is antimony sesquisulphide— Sb_2S_3 . Allow the precipitate to subside, pour away the clear liquid, and divide the remaining sulphide between two test-tubes.

a. Add to the precipitate in one of the tubes some strong hydrochloric acid and boil. Note that the sulphide dissolves and H_2S gas is evolved, as in the solution of the native sulphide.

b. Add to this portion ammonium hydrate; the sulphide does not dissolve, unlike the corresponding arsenic sulphide, but when some yellow ammonium sulphide is added solution takes place, even in the cold, but more easily when the mixture is warmed. The solution thus obtained again affords the sulphide when acidulated with hydrochloric or other acid.

The sulphide obtained artificially is amorphous and hydrated, but it gradually loses water and becomes crystalline and as nearly black as the native sulphide, with which it is then identical in composition. The

¹ *It is doubtful whether this body is either a basic or acid-forming oxide,*

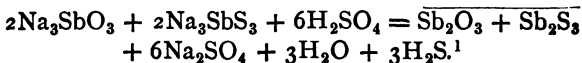
solubility of the sulphide in alkaline sulphide is due, as in the case of arsenic sesquisulphide, to the formation of a sulphur salt or ammonium sulphantimonite, which latter is easily decomposed by acids. An unimportant pentasulphide— Sb_2S_5 —is known.

A mixture of oxide and sulphide of antimony is used in medicine under the name of *Sulphurated antimony*, and is prepared in the following way, according to the directions of the British Pharmacopœia.

Experiment 386.—Boil in a porcelain dish ten grams of finely-powdered native antimony sulphide with fifty cubic c.ms of caustic soda solution, B.P., adding water from time to time in order to compensate for evaporation. Most of the sulphide dissolves, and the solution contains sodium antimonite and sulphantimonite :—



Pour off the hot solution from any insoluble matter and add to the liquid diluted sulphuric acid with frequent stirring until the mixture reddens litmus paper; an orange-red precipitate is obtained, which is to be collected on a filter, washed with water and dried at 100°C . This is a mixture of sulphide and oxide resulting from a decomposition of the kind indicated by the equation—



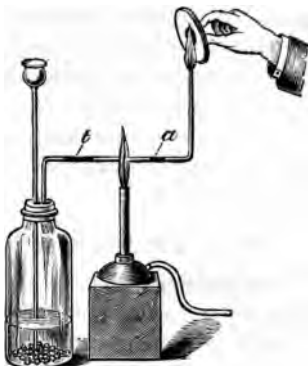
Only a portion of the H_2S is evolved as gas, as much of it

The orange-red powder resulting is the *Kermes mineral* of the older chemists.

Experiment 387.—Arrange a gas bottle as in Marsh's test for arsenic, or fig. 116, but add to the contents some tartar emetic solution, while gas is being steadily evolved

FIG. 116.

and burning at the jet. Shortly after the addition of the antimonial solution the flame is seen to alter in colour to a pale lavender-blue tint, and white smoke issues from it. On depressing the porcelain crucible lid on the flame a dull black deposit forms on it, and the delivery-tube, if treated as in testing for arsenic, becomes similarly coated.

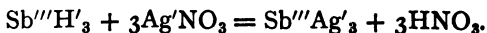


Pour some solution of bleaching lime over the deposit on porcelain, and note that it is scarcely affected by this liquid, which, as we have already seen (Experiment 367), rapidly dissolves arsenic. Now wash off the bleaching lime, and pour over the film some *yellow* sulphide of ammonium; note that the deposit easily dissolves in the reagent, owing to the

reagent reacts with the Sb_2O_3 , resulting from the decomposition of the antimonite by the acid, and converts it into Sb_2S_3 ; hence the final product contains much less Sb_2O_3 than is indicated by the gravimetric estimation.

formation of sulphantimonite. The two effects serve to completely distinguish the antimonial from the arsenical film.

The body which affords the antimonial deposit in the above case is *hydrogen antimonide*, $\text{Sb}''' \text{H}'_3$, analogous to AsH_3 , and similarly produced by the action of nascent hydrogen. We already know that $\text{As}''' \text{H}'_3$, when passed through solution of silver nitrate, affords a black precipitate of metallic silver (see Experiment 367). On testing the antimonial hydride in the same way a dark precipitate is also obtained ; but this is found on analysis to consist of silver antimonide, $\text{Sb}''' \text{Ag}'_3$.



Experiment 388.—Repeat Fleitmann's test (see Experiment 368), but using an antimonial solution instead of an arsenical one. No discolouration of the silver nitrate paper is observed, for the antimony hydride, unlike that of arsenic, is not formed in the alkaline liquid, and pure hydrogen alone is given off, which does not affect the silver salt. This test, therefore, serves to distinguish antimony from arsenic with great ease.

Experiment 389.—Apply Reinsch's test (see Experiment 369) to an antimonial liquid ; note that the copper assumes a gray metallic coating, but when the coated copper is dried and heated in a glass tube it does not afford the easily-recognised crystals of As_2O_3 ; if, however, the copper be boiled in a weak solution of caustic soda slightly coloured with a drop of potassium permanganate (Odling), a liquid is ob-

tained which, when poured off from the copper into a clean test-tube and acidulated with hydrochloric acid, gives the usual orange-red precipitate of Sb_2S_3 with sulphuretted hydrogen. In this case the antimony electro-chemically deposited on the copper is oxidised by the permanganate, and then dissolves in the caustic soda, forming therewith the soluble antimonite.

Antimony is detected in *cases of suspected poisoning* by the methods of Marsh and Reinsch, conducted as in the examination for arsenic, with the modifications above indicated.

Experiment 390.—Add to a solution of ‘tartar emetic’ in a test-tube a small quantity of a solution of *tannin* in water. Note that a precipitate forms of so-called ‘tannate of antimony.’ Tartar emetic solution is precipitated by any liquid containing tannin, such as tea, coffee, or decoction of oak bark, and these liquids are in consequence employed as *antidotes* in the treatment of antimonial poisoning.

Soluble antimonial compounds are highly poisonous, and have frequently caused death. The chloride exerts a powerful corrosive action, in addition to the special effects due to absorbed antimony. The symptoms caused by tartar emetic are very characteristic; these are extraordinary depression and frequent fainting, violent vomiting (which in some degree helps the elimination of the poison), and diarrhoea, leading to collapse and death.

The special treatment to be adopted is indicated by the above experiment. Vomiting is to be encouraged, while warmth and stimulants are employed to maintain the heart's action and help the circulation.

■

CHAPTER XXVIII.

EXPERIMENTS WITH BISMUTH AND ITS COMPOUNDS.

BISMUTH.—*Symbol* $\text{Bi}^{\text{v}}=210$.¹ The element bismuth is met with in comparatively small quantities in nature, but is usually found in the free state. Its extraction from a rich ore consists in melting out the easily fusible bismuth from the much less fusible earthy and other mineral substances with which it is associated. A portion of the bismuth met with in commerce is obtained as a secondary product in the treatment of some ores of other metals—chiefly those of lead, tin, and silver—in which it occurs in small quantity.

Whatever the source of the element may be, the specimens commonly obtainable are nearly pure, but usually contain a small proportion of arsenic. This impurity does not affect the value of this material for use in the arts, but compounds of bismuth are used in medicine, and arsenic must, of course, be carefully excluded from these bodies; hence the British Pharmacopœia gives the following process for the purification of commercial bismuth:—

Experiment 391.—Fuse common bismuth with one-tenth of its weight of nitre in a small Hessian crucible, stir the fused materials together until the *nitre solidifies*, although the heat is maintained. Now

¹ *The weight whose heat capacity is equal to 108 of silver.*

remove this crust and add a similar proportion of fresh nitre and treat as before. Finally, pour out the bismuth on a cold slab and let it solidify. In this treatment the fused nitre oxidises the arsenic, and removes it as potassium arsenite and arsenate, while some of the bismuth also oxidises and contributes to the formation of the crust.

Note that the bismuth, either purified as above or as usually met with, resembles antimony in lustre and colour, though it has a distinct rosy tint ; its specific gravity is sensibly greater than that of antimony (9.8 if water $= 1$), but like the latter it is very brittle, easily powdering under the hammer, and is highly crystalline in structure. It is a good conductor of electricity and heat, and, so far as these characters are concerned, is evidently a well-marked metal. It fuses at the low temperature of 270° C. ; hence alloys containing bismuth should be easily fusible.

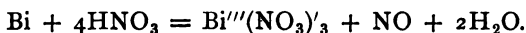
Experiment 392.—Mix in a small clay crucible 2 parts of bismuth, 1 of tin, and 1 of lead ; melt at a gentle heat. When quite liquid mix well and pour out on a cold slab. The product resembles common plumber's 'solder' in appearance. Throw a piece into some water contained in a test-tube and boil ; note that the alloy melts in the boiling water, therefore its fusing point must be lower than 100° C. If a thermometer be immersed in the water so that its bulb shall be in contact with the alloy, and the heat be slowly applied, it will be found that when the thermometer reaches 94° C. the alloy begins to melt.

This is the alloy termed fusible metal, but if half the tin in the above be replaced by the same weight

of cadmium an alloy termed Wood's metal is obtained, which begins to melt at 60° C. These alloys are much used for taking casts of dies, woodcuts, &c., for which purposes they are well suited, as they expand at the moment of solidification, and thus afford sharp impressions. It may be added that they are sometimes used by conjurors to make teaspoons which melt and disappear in hot liquids.

Bismuth is readily attacked by nitric acid, but not by hydrochloric; hence we shall examine its action with the former.

Experiment 393.—Pour some moderately strong nitric acid over metallic bismuth contained in a porcelain dish, and note that chemical action soon takes place, the metal gradually disappearing; add sufficient acid to secure complete solution, then heat the contents of the dish in order to evaporate any great excess of acid used. When the concentrated solution is allowed to cool, it slowly deposits crystals of bismuth nitrate, $\text{Bi}'''(\text{NO}_3)'_3, 3\text{H}_2\text{O}$, in which compound the metal evidently acts as a triad, replacing three atoms of hydrogen—



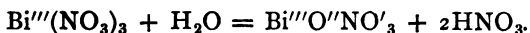
Redissolve the crystals by heat, and pour the liquid into about 100 times its volume of water, then stir well and note that a white precipitate forms immediately. Filter the turbid mixture,¹ wash the precipitate with some water, then dry it at a temperature not exceeding 66° C. ($=150^{\circ}$ F.).

¹ *The liquid that passes through the filter is highly acid and still holds some bismuth in solution; the latter can be easily removed, as in Experiment 394.*

The composition of the heavy white powder thus obtained is represented by the formula—



The derivation of this body from the soluble nitrate by the action of a large excess of water is shown in the following equation, excluding the water of hydration in each case :—



This change is analogous to the decomposition of SbCl_3 by water, observed in Experiment 379.

The insoluble white body so formed is termed 'subnitrate of bismuth' in the British Pharmacopœia, whose directions we have followed in its preparation.

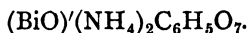
On comparison of the formulæ of the two nitrates of bismuth, it is evident that the first body is to be regarded as the normal nitrate of the triad metal, whereas the 'subnitrate' may be viewed as the nitrate of a monad group ($\text{Bi}'''\text{O}''$)' or bismuthyl, analogous to the group ($\text{Sb}'''\text{O}''$)' or stibonyl (see Experiment 379). The importance of recognising the existence of the bismuthyl group will appear in the course of our next experiment.

Experiment 394.—Instead of pouring the solution of bismuth nitrate into water, as in the last experiment, add it gradually and with constant stirring to a dilute solution of ammonium carbonate, collect and wash the precipitate formed, and dry as before. The product is a white powder, which effervesces abundantly when treated with nitric acid; it is therefore a carbonate, and its composition is represented by the empirical formula $(\text{Bi}_2\text{CO}_3)_2\text{H}_2\text{O}$. The compound is termed 'carbonate of bismuth' in the British

Pharmacopœia, but the formula of true carbonate of bismuth should be $\text{Bi}'''_2(\text{CO}_3)''_3$. If, however, we regard the body as hydrated bismuthyl carbonate $((\text{BiO})'_2\text{CO}_3)_2\text{H}_2\text{O}$ all difficulty disappears.

Experiment 395.—A soluble bismuth compound analogous in some respects to *tartar emetic*—in constitution not in therapeutic properties—is now much used in medicine. It is termed in the British Pharmacopœia ‘solution of citrate of bismuth and ammonia,’ or *liquor bismuthi*. In order to prepare a small quantity of the solution, take one gram of bismuth, dissolve in nitric acid and evaporate off excess, dilute with a little water, and add two grams of crystallised *citric acid* previously dissolved in the least possible quantity of water; then add gradually to the mixture some ammonium hydrate until the precipitate formed is redissolved, and the solution is neutral or faintly alkaline to test-paper. Finally, dilute to the volume of twenty cubic c.ms, and a solution of pharmacopœial strength is obtained.

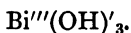
In this case the tribasic citric acid, $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$, prevents the precipitation of a bismuth compound on dilution with water or addition of alkali. The body formed in solution has the composition—



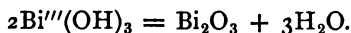
When hydrochloric acid is added to the solution, a precipitate of BiOCl is formed, which is soluble in excess of the reagent.

Experiment 396.—Again pour some bismuth *nitrate solution* into water containing ammonium, *potassium*, or *sodium hydrate*. A white precipitate

forms, which is not in any case soluble in excess of the reagent, and consists of bismuth hydrate—



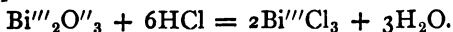
When this hydrate is washed, dried, and heated gently, it loses water, and a residue of bismuth sesquioxide is obtained—



The carbonate prepared as in Experiment 394 loses water and carbon dioxide gas on heating, and a residue of the oxide is obtained. This anhydrous oxide is a yellowish powder, which fuses at a red heat. It dissolves in nitric acid and reproduces the nitrate.

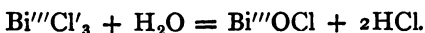
Experiment 397.—Add a small quantity of bismuth oxide to strong sulphuric acid in a test-tube and warm. Note that the oxide dissolves and the solution bears free dilution with water in presence of an excess of sulphuric acid without producing a precipitate. When the solution is carefully evaporated in a capsule, a saline mass is left which contains the compound $\text{Bi}'''_2(\text{SO}_4)''_3$. Hence bismuth forms a true sulphate as readily as antimony.

Experiment 398.—Dissolve some bismuth oxide in hydrochloric acid; solution is easily effected, and the liquid contains the trichloride—



If the strong solution be subjected to distillation, as in Experiment 378, with the corresponding antimony compound, water and free acid pass over first, and at the end of the operation the fused trichloride is obtained, which easily sublimes in good crystals. When the solution of the trichloride is diluted with

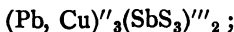
large volume of water a white precipitate is obtained analogous to antimony oxychloride ; thus—



The bismuth oxychloride thus formed is almost absolutely insoluble in water.

Experiment 399.—Pass sulphuretted hydrogen gas through, or add aqueous solution of the gas to, any of the above liquids containing dissolved bismuth, but free from any considerable excess of acid. Note that a black or brownish-black precipitate is formed, which consists of Bi_2S_3 , a body which is also found native in small quantity as *bismuth glance*. This sulphide is insoluble in dilute acids, alkalies, and alkaline sulphhydrates; in this last particular differing materially from the corresponding arsenic and antimony sulphides, *q. v.* The compound is, however, easily attacked and dissolved by moderately strong nitric acid, a nitrate of bismuth resulting, while much of the sulphur oxidises.

Although bismuth sulphide does not dissolve in alkaline sulphhydrate with the production of soluble sulpho-bismuthites, we are acquainted with several well-defined minerals in which bismuth may be regarded as a constituent of the acidic group. The best known compound of this kind is *needle ore*, or *aithenite*, whose composition is $(\text{Pb}, \text{Cu})''_3(\text{BiS}_3)'''_2$.¹ This body is chemically analogous to the corresponding sulphantimonite named *bournonite*—

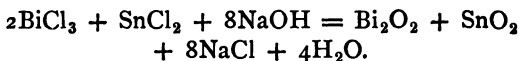


¹ *Some of the copper is usually replaced by lead, and this is indicated by bracketing the symbols.*

and we are acquainted with a compound termed *kobellite*, in which a portion of the antimony of a sulphantimonite is replaced by bismuth, in accordance with the law of isomorphism. The formula of *kobellite* may be written $\text{Pb}''_3[(\text{Bi}, \text{Sb}), \text{S}_3]'''_2$. Hence we recognise in bismuth sulphide the existence of the acidic function, but in a much lower degree than in the cases of arsenic and antimony. On the other hand, the basic properties are much more strongly marked in bismuth; and the latter thus brings us to the metallic side of this group of elements.

When bismuth solutions are treated with reducing agents no compound analogous to PH_3 , AsH_3 , or SbH_3 is obtained, but reduction either to metal or a lower oxide than Bi_2O_3 takes place. Reduction of the latter kind is effected in the following way:—

Experiment 400.—Mix solutions of BiCl_3 and stannous chloride, SnCl_2 , and add to the mixture caustic soda or potash in excess. A precipitate is formed which is nearly black if sufficient stannous chloride has been added, but is often streaked black and white.¹ The black precipitate is an oxide of bismuth, Bi_2O_2 , named bismuthous oxide, and is thus formed—



If considerable excess of caustic soda be added, the stannic oxide, or rather hydrate, actually formed

¹ In consequence, this is sometimes termed the magpie test for bismuth; the reaction serves easily to distinguish the latter from lead,

dissolves in the alkali, and leaves the bismuthous oxide, which is a feeble base. This oxide burns in air, and forms the sesquioxide.

Experiment 401.—Suspend some Bi_2O_3 in very strong solution of caustic potash contained in a test-tube, and pass chlorine gas into the mixture while the vessel is heated. The oxide assumes a reddish-yellow colour, which soon passes to blood red, and a powder deposits, and can be collected by decantation after diluting the liquid. This powder is washed with water, and then treated for a short time with dilute nitric acid, to remove any unaltered sesquioxide or alkali; it may be then collected and gently dried.

The red powder when pure has the composition HBiO_3 , and is a bismuthic acid analogous to metaphosphoric acid.

When the red powder is gently heated to 120°C . it loses water and is converted into bismuth pentoxide, Bi_2O_5 (the analogue of phosphorus pentoxide), a brownish-red powder, which, if again heated to 150°C ., gradually loses oxygen and is reduced to Bi_2O_4 (the analogue of Sb_2O_4). The compound Bi_2O_4 , when more strongly heated, loses an atom of oxygen, and is finally reduced to the sesquioxide Bi_2O_3 .

Bismuth acids analogous to pyro- and orthophosphates are said to exist, but little is yet known about them.

Although bismuth is triad in most of its compounds, the existence of the group of bodies just *referred to is good evidence of the pentad character of the element in some of its relations, while through-*

out numerous analogies are traceable between certain of its derivatives and those of the other members of the class to which phosphorus and arsenic belong.

This group of pentads includes the three rare metals VANADIUM = 51·2, whose chief mineral compound is *vanadinite*, a chloro-vanadate of lead, which exactly corresponds in constitution¹ to mimetesite and pyromorphite, and crystallises in the same system ; TANTALIUM = 182 ; and NIOBIUM = 94, which occur together in several natural compounds, but chiefly in combination with iron in the very rare minerals *tantalite* and *columbite*.

¹ As Roscoe has shown in the course of his fine researches in Vanadium.

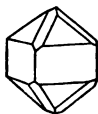
CHAPTER XXIX.

EXPERIMENTS WITH TIN AND ITS COMPOUNDS.

TIN, Sn^{117} (*Stannum*)=118. We have already used one of the compounds of this element, in Experiment 400, to aid in the production of a low oxide of bismuth, and it is now convenient to examine the metal itself and its products for another reason, namely, that it is closely related to the last group of elements considered, though commonly acting as a tetrad or diad. In fact, tin stands almost alone amongst the well-known metals, and has even been denied admission to the class of metals, owing chiefly to its feebly-marked basic characters, and the strong resemblance between some of its compounds and those of silicon.

Tin is not certainly known to occur in the pure state in nature, but is obtained from its chief mineral compound *tinstone*, whose composition is SnO_2 . This

FIG. 117.



mineral, which is often met with in dark and lustrous crystals, resembling fig. 117, is found in comparative abundance in different parts of the world, in Australia and the Island of Banca, for instance, while its chief British

locality is Cornwall.

Experiment 402.—Break up and powder a tolera-

bly pure specimen of native *tinstone*, mix it with rather more than its own bulk of powdered charcoal, and introduce the mixture into a small Hessian or clay crucible; then cover with a thick layer of 'bread soda,' and gradually heat the crucible to full redness in an ordinary fire. When the contents of the crucible have been in quiet fusion for some time, remove from the fire, allow the contents to cool, and break the vessel. If the operation has been properly conducted, a silvery-white button of tin will be obtained.

The process followed on the large scale for the reduction of tin is substantially the same as that just used, but roasting of the crude ore for the removal of arsenic and sulphur precedes reduction, and the reducing agent is anthracite coal instead of charcoal. Pure metallic tin is a silver white metal of brilliant lustre. Its specific gravity is 7.3 (water=1). When a strip is bent it emits a crackling sound.

Experiment 403.—Melt some tin in an iron ladle; it liquefies far below a visible red heat—that is to say, at 235° C.—and, when melted, easily oxidises and becomes covered with a grey scum of oxide. At a very high temperature the metal burns vigorously, and produces flocks of its oxide, which were often termed by the alchemists *Flores stanni* or *Jovis*. For our immediate purpose, however, it is unnecessary to raise the temperature above the melting point; the liquid is then to be poured out into an iron mortar. The metal solidifies, but if quickly beaten with a pestle before its temperature has fallen below 200° C. it quickly falls to powder, and fine *grain* or *powdered tin* is thus easily obtained. In

the cold, or at temperatures well below 200° , the metal is very malleable, and can be rolled into sheets. Ordinary *tin-foil* is thin sheet tin thus rolled; it usually contains a little lead.

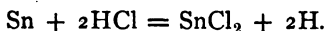
Ordinary mirrors, or looking-glasses, are prepared with this tin-foil, which is laid on a flat surface and covered with mercury; the glass plate is laid upon the mercury, and the excess of the latter is squeezed out, when a solid *amalgam* of tin and mercury remains, which adheres firmly to the glass, and produces the brilliant reflecting surface we are accustomed to employ.

Common tin-plate is produced by dipping iron sheets, previously cleaned by scouring with a dilute acid, into molten tin, which then adheres to the surface. Copper articles are also tinned by dipping. In each case a superficial alloy of tin with iron or copper is probably formed, while externally the coating is pure tin.

The fine white *speculum metal* used in the construction of the mirrors for astronomical telescopes is an alloy of two parts of copper and one of tin; *bell-metal* contains four or five parts of copper and one of tin; *gun-metal*, nine of copper to one of tin; and the *bronze* used in our new copper coinage consists of copper ninety-five parts, tin four parts, and zinc one part. Some samples of bronze contain as much as four parts of zinc.

Good *pewter* is an alloy of four parts tin and one of lead; common *plumber's solder* consists of equal parts of tin and lead, while *Britannia metal* contains tin, copper, zinc, and a little antimony and bismuth.

Experiment 404.—Heats some granulated tin with strong hydrochloric acid¹ in a flask for an hour or so, and gradually evaporate until crystals begin to form in the hot liquid. Hydrogen is evolved during solution of the tin. On cooling the liquid, fine prismatic crystals separate, and these consist of hydrated stannous chloride, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$; when these crystals are dried *in vacuo* over oil of vitriol they lose all the water, and the compound SnCl_2 remains. The reaction of tin with hydrochloric acid is thus represented—



The hydrated chloride is identical with the dyer's *tin salt*,² and is obtained in quantity by the above process.

The compound is easily soluble in water, but when largely diluted and exposed to the air, a more or less hydrated basic chloride, $\text{Sn}''\text{Cl}'(\text{OH})'$, separates, and renders the liquid opalescent. The iodide and bromide of tin analogous to the above chloride are known.

Experiment 405.—Repeat Experiment 400 with bismuth solution and excess of alkaline hydrate; the *black* precipitate of bismuthous oxide is obtained.

Experiment 406.—Pass a current of chlorine gas into the solution of the tin chloride until the liquid has the odour and colour of the chlorine. Now test a portion of the liquid with bismuth chloride and

¹ Solution is facilitated by electro-chemical action when a few small pieces of platinum foil are thrown in with the tin.

² Used as a *mordant*; see page 55.

alkali as before, and note that a *white* precipitate ultimately formed. When the solution charged with chlorine is cautiously evaporated, a crystalline body separates, whose composition is $\text{SnCl}_4, 3\text{H}_2\text{O}$. This body obviously results from the addition of chlorine to the compound SnCl_2 , thus, excluding water—



We, therefore, recognise two chlorides of tin, a di-chloride and a tetrachloride, the former easily passing into the latter, and the two bodies being readily distinguished by the bismuth test.² In fact, the di-chloride acts as a reducing agent for the bismuth salt, owing to its tendency to pass into the tetrachloride. For a similar reason it is used in the arts as an *anti-chlore*.³

The first chloride, SnCl_2 , is termed *stannous chloride*, and is the type of compounds in which the atom of tin acts as a *diad*. The higher compound, SnCl_4 , is named *stannic chloride*, and is the type of another class of compounds in which the tin atom acts as a *tetrad*. Stannous readily passes into stannic compounds, and therefore act as powerful reducing agents.

When tin is dissolved in hydrochloric acid, to which nitric acid is added from time to time, a solution of the tetrachloride is obtained, and this, when evaporated, affords the so-called *nitromuriate of tin*

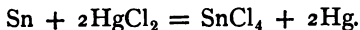
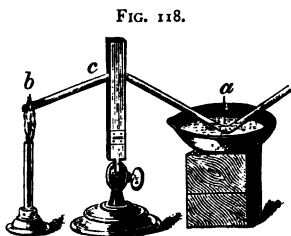
¹ If solution of iodine be gradually added, instead of chlorine, the former is decolourised as long as SnCl_2 is present.

² See also under Experiment 400.

³ See Part II., under Experiment 311.

(really hydrated tetrachloride), which is employed by dyers for brightening and fixing red colours on fabrics.

Experiment 407.—We can easily prepare the anhydrous stannic chloride in the following way: Mix intimately in a mortar one gram of powdered tin with four grams of corrosive sublimate or mercuric chloride, HgCl_2 —a very poisonous body that must be handled with *great care*. Introduce the mixture into a long glass tube closed at one end; then bend to the form shown in fig. 118, immerse the bend *a* in a capsule containing cold water, and heat the mixture at *b*. A colourless fuming liquid distils over and condenses in *a*, while droplets of mercury collect in the cooler part about *c*. The colourless liquid is pure stannic chloride, thus formed—



Stannic chloride boils at 115°C. ; its specific gravity in the liquid state is 2.267 (water=1); it absorbs moisture from the air, and forms hydrates, which do not again part with water without decomposition. As already observed, the hydrates dissolve and bear mixture with a considerable proportion of water without forming a precipitate; but on boiling the dilute liquid a yellowish white body separates, which is a *hydrate of the metal*.

An iodide and a bromide corresponding to the chloride SnCl_4 have been obtained; but the tetrafluoride has not been isolated. Several derivatives of the latter are known, however, and the compound K_2SnF_6 is easily obtained by the action of hydrofluoric acid on potassium stannate (see under Experiment 409). This body is obviously analogous to potassium silicofluoride K_2SiF_6 .

Experiment 408.—Add to a fresh aqueous solution of *stannous* chloride, SnCl_2 , sodium hydrate drop by drop. Note that a white precipitate is produced; this is a *stannous hydrate*, whose formula is $\text{Sn}_2\text{O}_3\text{H}_2$, which may be written—



This body quickly absorbs oxygen from the air, but before it has time to do so, add more alkali until the precipitate is partly redissolved,¹ and then boil the mixture. On heating, the precipitate sensibly darkens in colour, some of the dark anhydrous *stannous oxide*, SnO , resulting. The latter, when dry and heated in the air, burns and produces the yellowish compound, SnO_2 , or *stannic oxide*.

Stannous hydrate dissolves in acids and forms salts, *e.g.* in dilute sulphuric acid, forming the sulphate SnSO_4 .

Experiment 409.—Treat a solution of *stannic* chloride, SnCl_4 , as in the last experiment; a precipitate is formed which does not darken in colour on

¹ Stannous hydrate can be completely redissolved by addition of excess of the caustic soda, and the resulting liquid is a powerful reducing agent.

boiling, but dissolves if excess of sodium hydrate be added to the hot liquid and the digestion continued.

The precipitate formed in the first instance has the formula H_2SnO_3 , and from its solution in excess of caustic soda the compound $\text{Na}_2\text{SnO}_3, 3\text{H}_2\text{O}$ can be crystallised out. Hence the hydrate is a true acid termed *stannic acid*, which forms the salt *sodium stannate*. A corresponding soluble potassium salt can be obtained in a similar way, but other stannates are insoluble.

Sodium stannate is largely used by dyers in the manner indicated below, and is prepared for this purpose by fusing native tinstone with caustic soda, dissolving the product in water, and crystallising out the tin salt.

Sodium stannate is employed in dyeing and calico printing as a *mordant*. Technically its solution is termed *prepare liquor*, because it prepares the cloth to hold the dye; for when the tissue is steeped in a dilute solution of the stannate, the latter is decomposed by the fibre and stannic hydrate deposited upon it. The dye materials used, though little disposed to attach themselves directly to the fibre, are readily attracted and held by the stannic hydrate, which may be thus said to 'bite in' the colour, or to act as a *mordant*.¹

Experiment 410.—To the alkaline stannate solution obtained in the last experiment add hydrochloric acid cautiously as long as the precipitate first formed increases in bulk;² we thus get the stannic acid back.

¹ From the French = 'biting.'

² An excess would, of course, redissolve the precipitate and

Now throw the mixture on a filter, and wash the hydrate with water; this is a very slow operation, but when completed, dry the precipitate, detach it from the filter, and heat to redness in a porcelain crucible. The residue is deep yellow when hot, and a very pale tint when cold; it is quite insoluble in water, and in most acids.

This body is the pure dioxide, SnO_2 , in the amorphous condition, and is identical in composition with native tinstone or *cassiterite*. The oxide is also formed by heating molten tin in contact with air; thus prepared, it is termed *putty powder*, and is much used for polishing glass, stone, and steel. The oxide, when fused with glass, converts the latter into a white and nearly opaque *enamel*.

Experiment 411.—Pour some strong nitric acid over tin contained in a capsule; ruddy fumes are evolved, and the metal is wholly converted into a yellowish-white powder, which does not dissolve in excess of acid. Wash the powder with water in order to free it from nitric acid. The product, when air-dried, consists of H_2SnO_3 , and therefore has the same composition as the stannic acid already obtained; it differs from the latter in being only slightly soluble in caustic alkali, and insoluble in nitric acid; but it is dissolved by strong hydrochloric acid. In the last case, however, combination appears to be effected, and the product is soluble with great ease when much water is added. This variety of H_2SnO_3 is termed *metastannic acid*, and a number of metastannates reform the stannic chloride in solution. The hydrate is also dissolved by dilute nitric acid.

have been obtained from it, but of such complicated constitution that there is little doubt metastannic acid is a polymer of stannic acid or $n\text{H}_2\text{SnO}_3$, but the value of n is not definitely known.

When metastannic acid is heated to redness water is expelled, and SnO_2 left, which is indistinguishable from that obtained in the last experiment.

Experiment 412.—Add to solution of *stannous* chloride some sulphuretted hydrogen water, and note that a nearly *black* precipitate is formed; the compound thrown down is more or less hydrated stannous sulphide, SnS , which is insoluble in dilute acids.

Experiment 413.—Perform a similar experiment with *stannic* chloride solution; a pale *yellow* precipitate is formed of stannic sulphide, SnS_2 , which is insoluble in dilute acid. Allow the precipitate to settle, pour off the supernatant liquid, and, having added enough ammonium hydrate to neutralise any free acid present, pour in some yellow ammonium sulphhydrate solution, and warm. The SnS_2 dissolves, and the solution contains the ammonium salt of sulphostannic acid.¹ From this solution acid reprecipitates the yellow stannic sulphide along with some sulphur.

Stannous sulphide also dissolves in yellow ammonium sulphhydrate, but it unites with another atom of sulphur derived from the reagent and forms the sulpho-stannate, as before. The solution then affords a *yellow* precipitate of SnS_2 when acidulated.

A crystalline variety of stannic sulphide termed

¹ Tin pyrites, which is occasionally met with in nature, is a salt of the sulphostannic H_4Sn_4 , in which copper, iron, and zinc replace the hydrogen of the acid,

aurum mustivum, or *mosaic gold*, is employed as a 'bronze powder.' It is prepared by heating to low redness in a flask a mixture of 15 parts of a powdered amalgam of tin and mercury (containing 12 parts of tin to 3 of mercury) with 7 parts of sulphur and 3 of ammonium chloride. Vapour of mercury, ammonium chloride, and sulphur are given off, while part of the stannic sulphide formed sublimes; the rest is left in the flask. The sulphide exhibits the metallic lustre, and has a more or less golden-yellow colour. This preparation is better avoided, as the vapour of mercury is injurious to health.

The following rare metals are closely allied to tin, viz.—TITANIUM, $Ti^{iv}=48$, met with in titanite iron ore, or *ilmenite*, and in *rutile* TiO_2 (*anatase* and *brookite* are other crystalline forms of the same compound); THORIUM, $Th=231.5$, found in a silicate named *thorite*; and ZIRCONIUM, $Zr=90$, in *zircon*, or *hyacinth*, a mineral silicate of zirconium.

CHAPTER XXX.

THE NOBLE METALS.—EXPERIMENTS WITH PLATINUM.

THE experiments just made with tin and its compounds complete our study of the several elements whose claims to be classed as metals have been disputed by many chemists. We now have to examine the bodies whose membership of the metallic division is generally admitted, and in pursuing our inquiry we naturally deal first with those which are most electro-negative. Under Experiment 37 a list of metals is given arranged in an electro-chemical order, which is there stated to be subject to some variation when the comparisons are made under different conditions; but in all lists of the kind the metals gold, platinum, and silver appear on the *negative* side, or that approaching to the non-metals; hence, they next claim our notice. It is, perhaps, fortunate that the group of bodies just referred to should thus early occupy our attention, as they are popularly regarded as typical *metals*, and, in fact, do exhibit, in a high degree, the more easily observed metallic characteristics.

Gold, silver, and platinum have long been termed 'noble metals,' because they completely resist oxidation or rusting at high or low temperature, for they do not *directly* unite with oxygen under any circumstances, and thus cannot be 'debased.' Compounds

with oxygen can be indirectly obtained, but they are easily reduced by comparatively slight elevation of temperature. Of the three noble metals, platinum is a tetrad, like tin; gold a triad, and silver an apparent monad. Following this order we shall first examine—

PLATINUM,¹ $Pt^{1v}=196.7$.—This metal is always found in nature as the free element, either in grains, or small rolled masses, or ‘nuggets,’ scattered through the alluvial sands which are met with amongst the Ural mountains in Siberia. It is found in other parts of the world in small quantity, but the chief supplies of the metal are derived from Russia. The grains or rolled masses do not consist of the pure element, as small quantities of the rare metals palladium, iridium, osmium, rhodium, ruthenium, and occasionally gold, accompany the platinum.

Experiment 414.—Obtain a thin wire of platinum and heat it to the highest attainable temperature, either in a furnace or more conveniently in a strong blowpipe flame. In neither case does the platinum show any trace of fusion,² though the metal is evidently a bad conductor for heat, since one end of a short wire can be held in the fingers for a time, even though the other end be white hot.

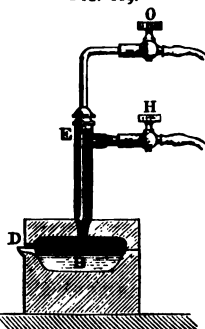
Substitute for the mouth blowpipe the oxyhydrogen jet, and note that the wire, when held in the flame, is easily melted. Advantage is taken of this fact by Deville in order to purify and cast platinum.

¹ ‘Little silver,’ from *plata*, the Spanish term for silver.

² If very thin the wire may soften and bend under its own weight. At a very high temperature pieces of platinum can be welded together by compression or hammering.

The crude material is placed in the lime furnace, shown in fig. 119. This furnace consists of a large block of lime (a material we already know from Experiment 65 to be infusible in the oxyhydrogen flame) cut in half, the centre scooped out so as to form a cavity, B, as shown, and a channel provided, as at D. The top of the furnace is drilled, in order to permit the passage of the compound jet E for the delivery of the two gases.

FIG. 119.



The crude metal, separated as far as possible by mechanical means from sand, &c., is introduced into B in small quantities at a time and fused. Most of the impurities are removed during fusion ; some, like osmium, being oxidised and vaporised ; others uniting easily with the lime of the furnace ; while the purified and molten platinum (still containing a little iridium and rhodium, which rather improve the quality of the metal than otherwise) is cast into suitable moulds.

Platinum, as thus obtained,¹ is a greyish-white metal of high specific gravity, 21.5 (water=1). It is very malleable, soft, and can be drawn into wire of considerable tenacity. Its power of resisting very high temperatures without fusion or other alteration renders the metal of great value in the construction of crucibles and other vessels employed in chemical

¹ For some properties of finely-divided platinum, see Experiments 418 and 419.

operations. On the large scale platinum stills are used in the concentration of oil of vitriol, as the acid does not attack the metal; but its great cost—five or six times that of silver—limits its application in the arts.

Platinum vessels should not be used in cases where an easily fusible metal can be reduced in them, as platinum easily forms alloys with lead, zinc, tin, &c.; moreover, easily reducible silicon, boron, phosphorus, or sulphur compounds should not be heated in platinum crucibles, as the elements just named unite with the metal; nor should potassium or sodium hydrates or nitrates be fused in such vessels.

Experiment 415.—Divide a small piece of platinum wire or foil in two parts; place each part in a distinct test-tube, and boil one with strong nitric acid and the other with strong hydrochloric acid. Note that the metal is not attached in either case.¹ Now pour the contents of one tube into the other, and note that the metal gradually dissolves, and a brownish solution is produced.

Evaporate the solution just obtained to dryness, then add a few drops of strong hydrochloric acid and evaporate on the water bath again until all free acid has been driven off; a very dark brownish-red crystalline mass is obtained, which is very deliquescent in moist air. The crystalline body has the composition $\text{H}_2\text{PtCl}_6, 6\text{H}_2\text{O}$ or $\text{PtCl}_4, 2\text{HCl} + 6\text{H}_2\text{O}$. This body is often termed platinum tetrachloride,² but is

¹ Certain alloys of platinum are soluble in acids—*e.g.* an alloy with lead is soluble in nitric acid.

² A hydrate of the true tetrachloride, $\text{PtCl}_4, 5\text{H}_2\text{O}$, can be obtained, but by a different and complex process.

more correctly named chloroplatinic acid, H_2PtCl_6 , for reasons that will shortly appear.

Experiment 416.—Add to a few drops of the platinum solution a little potassium chloride. Note that a yellow or reddish-yellow precipitate is formed. In very dilute solution the addition of some alcohol facilitates the separation of the precipitate. The composition of the latter is K_2PtCl_6 . When strongly heated this body leaves a residue consisting of one atom of platinum and two molecules of potassium chloride, two-thirds of the chlorine passing off as gas.

Experiment 417.—Make a similar experiment with sodium chloride; no precipitate is formed, but fine large orange-red crystals are obtained when the solution is evaporated; these contain the compound $\text{Na}'_2\text{PtCl}_6$, which is easily soluble in water and alcohol.

Experiment 418.—Repeat the experiment with ammonium chloride.¹ A pale yellow precipitate is formed, which contains $(\text{NH}_4)'_2\text{PtCl}_6$. This, like the potassium salt, is easily separated from any dilute liquids by addition of alcohol, in which it is insoluble.

When this compound is heated strongly in a porcelain crucible, metallic platinum only is left, but in a very porous condition, termed *spongy platinum*. This form of the metal is also obtained by evaporating the chloroplatinic acid solution to dryness and heating the residue to redness. It was by this latter method we obtained the asbestos coated with

¹ This salt, when added to the solution of true platinum tetrachloride (see note to Experiment 415) precipitates the yellow compound much more slowly than from the above *chloroplatinic acid*.

spongy platinum that we required for use in Experiment 308. Advantage was taken in that experiment of the property possessed by platinum sponge to determine the union of oxygen and sulphur dioxide gases; the precise *modus operandi* of the platinum in that reaction is not yet understood, but is probably connected with the power which the rather finely divided metal is known to possess of condensing gases in its pores just as charcoal does (Experiment 225).

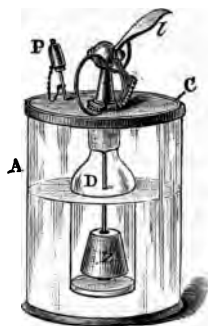
Experiment 419.—Squeeze together the particles of some spongy platinum obtained as in the last experiment, and enclose the little coherent mass in a loop or cage of thin platinum wire. Now hold the sponge in a stream of hydrogen issuing from a very fine jet, and the platinum will soon become red-hot,

and the gas will be inflamed.

This is the principle of the DOBEREINER lamp referred to under Experiment 53. Fig. 120 represents one of these lamps. The outer vessel A is a glass cylinder containing diluted sulphuric acid; the loose brass cover for the cylinder c carries the bottle D, which has no bottom; in this is suspended, by means of a wire, the lump of zinc z.

When the acid rises in D hydrogen is evolved, which has no exit save through the fine jet J, through which it is allowed to pass on depressing the lever l. The stream of gas then impinges on some platinum sponge, P, enclosed in the little cage. The metal

FIG. 120.



becomes red-hot and inflames the gas, which may then be used to kindle any other combustible body. On removing pressure from the lever, the gas no longer issues, and then accumulates in D until the acid is forced down out of contact with the zinc, when action ceases, and the apparatus may be put aside until again required.

Experiment 420.—Add to some of the platinum solution obtained, as in Experiment 415, a few grains of white sugar, then solution of sodium carbonate until the liquid is alkaline, and boil. A black substance separates, which is collected on a filter, well washed and dried. The black powder thus obtained is platinum in a still more finely divided condition than in the sponge, and possesses in a still higher degree the property of condensing gases and effecting their combination. This variety is termed *platinum black*. It is used in organic chemistry in facilitating oxidation at the expense of atmospheric oxygen.

Experiment 421.—Evaporate some more of the chloroplatinic acid solution to dryness in a wide test-tube, and heat the vessel cautiously to about 300° C. by plunging the closed end in oil heated in a cast-iron vessel to the requisite temperature.¹ Chlorine is evolved, and a greenish-brown residue left which does not dissolve in water or in dilute nitric acid, but dissolves in strong hydrochloric acid. The greenish solid has the composition PtCl_2 , and is *platinous* chloride, while its solution in hydrochloric acid, pre-

¹ Noted by means of a thermometer plunged in the oil.

pared in the absence of air, contains *chloroplatinous acid*, H_2PtCl_4 .

When PtCl_2 dissolves in hydrochloric acid in presence of air, chloroplatinic acid, H_2PtCl_6 , is obtained as before.

The oxygen compounds of platinum are not sufficiently important for direct experiment in this course, but it is desirable to state that platinous hydrate, $\text{Pt}(\text{OH})_2$, can be obtained by boiling the chloride PtCl_2 with potassium hydrate; and from $\text{Pt}(\text{OH})_2$ the corresponding oxide PtO is prepared by cautious heating. By similar treatment the higher chloride can afford $\text{Pt}(\text{OH})_4$, from which the oxide PtO_2 is obtained by gentle heat.

Experiment 422.—Pass sulphuretted hydrogen gas through solution of chloroplatinic acid; a black precipitate of PtS_2 is formed, which changes to brown on standing.

Note that the black precipitate, when washed, dissolves in yellow ammonium sulphide, since the metal forms a soluble sulpho-platinate. The latter is easily decomposed by acids, and the sulphide again separated.

Although it is usual to assume platinum to be a tetrad in platinic and a diad in platinous compounds, it is impossible to explain the constitution of chloroplatinic acid, H_2PtCl_6 , unless we assume either the metal to be an *octad* or chlorine polyatomic, and probably three-linked or triad. We prefer the latter *hypothesis*, as the study of certain organic chlorine compounds favours the view that in some few cases

CHAPTER XXXI.

EXPERIMENTS WITH GOLD AND SOME OF ITS COMPOUNDS.

GOLD, Au''' (*aurum*)=196·2.—This metal is another of the very small number almost invariably met with in the free or uncombined state in nature. Since it is the chief medium of exchange in the commerce of the world, a gold coin may be taken as the representative of the pure element. The British sovereign or half-sovereign is a rich alloy consisting of 11 parts pure gold and 1 part copper, the latter metal being used to give hardness to the alloy, as pure gold is too soft to resist the wear and tear of the constant use to which coin is subjected. The metal of which gold articles of jewellery are made is rarely as rich as the coin of the realm. The goldsmith speaks of the metal he employs as so many 'carats ¹ fine,' meaning thereby the number of carats of pure gold in 24 carats of metal. Thus 18-carat gold contains only 18 of the precious metal in 24 of alloy, the remaining 6 carats usually consisting of copper or silver, or a mixture of both metals: 15-carat and 9-carat fine contain respectively 15 and 9 of pure gold in 24 of alloy. On this scale pure gold would obviously be 24-carats fine. The only form in which the student can usually obtain pure gold is in the condition of the gold leaf used

¹ One carat = four grains.

by gilders, and commonly sold at a small price in little paper books. These golden films¹ are obtained by beating or hammering out the sheets of metal between layers of thin parchment, and finally between 'goldbeater's skin,' which is a still finer animal membrane derived from the intestines of the larger ruminants. So malleable is pure gold that it can be beaten out to a film only $\frac{1}{280000}$ th of an inch in thickness. These films are so thin that they can transmit some light, which is of a greenish colour. Gold can also be easily drawn into such fine wire, that Faraday has estimated it to be possible to produce a wire of sufficient length to encircle the earth from the weight of gold in four sovereigns.

Experiment 423.—Crush up several leaves of gold until reduced to a small bulk, and insert in a little hole made in a piece of charcoal; then place over the metal a little powdered *borax*, and direct the flame obtained with a mouth blow-pipe upon the material. The borax is soon fused, and on urging the flame strongly for some time, the gold can be fused into a minute yellow bead. This evidently consists of unaltered gold, and is easily flattened under a slight blow of a hammer.

Experiment 424.—Add the fragment of gold to a handful of clay, throw the latter into a rather shallow dish, make the clay into a paste with water, and then place the basin, with its contents, under a water-tap, and let a steady but not violent stream of water run

¹ These films are used in gilding letters, picture frames, &c., for which purpose the surface is carefully coated with gilding 'size,' to which the metallic film adheres.

into the dish and overflow from it until the clay has been washed away ; then, on pouring off the remaining water, the sandy residue can be examined with a lens, and the fragment of gold will most probably be found, as the high specific gravity of the gold, 19·3 (water=1), as compared with that of the clay and sand particles (whose density rarely exceeds 2), prevents its being carried away in the current.

In *gold washing*, most of the metal is extracted from the alluvial deposits in which it is found native by a method analogous to the above ; the material is washed by running water, and the gold particles are picked out from the residue.

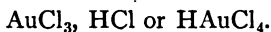
Gold is often met with disseminated through quartz rock, in which case the material is first crushed by powerful stamps, then washed with water, and the residue, after picking, is mixed with mercury, which dissolves the gold. From this *amalgam* the precious metal is obtained by distilling off the mercury. This process of *amalgamation* following the *crushing for gold* is illustrated by the following—

Experiment 425.—Place in a small crucible a few drops of mercury, and add to it a leaf or two of gold ; the latter is dissolved by the mercury.¹ On now applying heat to the crucible, the mercury is driven off, and a residue is left, which, when rubbed by a hard body exhibits the lustre and colour of gold.

Experiment 426.—Take two test-tubes and place a leaf of gold in each ; then into one pour strong

¹ *Dental amalgam* is obtained by adding as much gold to *mercury* as will suffice to give a pasty mass at the temperature of boiling water, but which can solidify on cooling.

hydrochloric acid, and into the other strong nitric acid, and warm in each case. The metal is not acted on by either acid, nor does any single acid, save the rare body selenic acid, act on gold. Now pour the contents of one tube carefully into the other, and back again, when the metal wholly disappears.¹ More gold leaf can be dissolved in the acid, and a yellow liquid is produced. If a little of the solution be placed in a porcelain capsule and evaporated nearly to dryness in the water bath, yellow crystals are obtained, whose composition is represented by the formula—



This body resembles chloroplatinic acid (Experiment 416) in forming well-crystallised salts; thus with potassium it affords the compound KAuCl_4 , or potassium chlor-aurate.

If, however, the crystals are gently heated, a molecule of HCl is driven off, and gold trichloride, AuCl_3 , remains, which is soluble in ether as well as water.

When the trichloride is heated to about 200°C . it parts with two atoms of chlorine, and a nearly white powder remains, which is insoluble in water. This body is gold monochloride or aurous chloride.



Thus the gold atom acts as a monad in the monochloride, a triad in the trichloride, and as an apparent pentad in chlorauric acid, if chlorine be monad.

Experiment 427.—To some of the solution of

¹ *Solution is due in this case to the action of the chlorine liberated. See Experiment 134.*

gold trichloride add a few drops of ferrous sulphate solution, and note that a brown precipitate is formed. This, when collected on a filter, washed and dried, easily assumes the lustre and colour of gold on rubbing with a hard body. The powder is therefore metallic gold in a fine state of division.¹ Thus the ferrous sulphate has reduced the gold trichloride.²

Experiment 428.—Add to a dilute solution of gold trichloride, having as little free acid as possible, a solution containing a mixture of stannic and stannous chlorides, or a mixture of stannous and ferric chlorides, also free from excess of acid. A purple precipitate falls, which is the *purple of Cassius*. This body is used as a pigment, especially in porcelain painting. It contains tin and gold, and is probably a mixture of stannic hydrate with gold in a still finer state of division than that obtained in the last experiment, and of a purple colour.

An oxide, Au_2O_3 , and its hydrate (the latter often termed auric acid) are known, these correspond to the trichloride; an aurous oxide, Au_2O , is also known. The following liquid, which can be used in *gilding*, probably contains at first potassium aurate, KAuO_2 .

Experiment 429.—Add a solution of potassium acid carbonate, KHCO_3 , commonly called 'bicarbonate of potash,' to solution of gold trichloride until all effervescence ceases, and a slightly alkaline liquid

¹ Solution of *oxalic acid*, aided by heat, also reduces a gold solution readily.

² See *IRON* for the explanation of the reducing action of ferrous sulphate.

is obtained. Then immerse in one portion of the liquid a clean strip of zinc, and in another portion a clean strip of copper, and boil the liquid in each case. If the original gold solution was strong enough, the zinc and copper, when removed from the solutions and polished, will be found coated with gold. Small metallic ornaments are thus easily gilt.

It is a solution of this kind which is commonly employed in *toning* photographic prints.¹ Metallic gold is reduced, as in the above instance, and covers the deposit which forms the shadows of the print with a more or less purple film, which is not only of a more pleasing tint than the layer of silver left after 'fixing' with sodium thiosulphate, but is less liable to change on exposure to atmospheric influences, and so protects the picture.

NOTE.—The student is recommended to carefully avoid the addition of *ammonia* to gold solutions, lest a highly-explosive body named *fulminating gold* should be produced.

Electro-gilding is effected by connecting the article to be gilt, after thorough cleansing, with the negative pole of a galvanic cell or battery and plunging into a gold solution, obtained by adding a considerable excess of the highly poisonous potassium cyanide to a neutral solution of gold trichloride. The positive pole is connected with a strip of gold, which is also immersed in the liquid. As the metal deposits on the object to be gilt, gold dissolves from the positive

¹ A double thiosulphate of gold and sodium is sometimes used for the same purpose.

plate, and thus maintains the liquid at the proper strength.

Experiment 430.—Pass a current of sulphuretted hydrogen gas through a dilute solution of gold trichloride, and a brown precipitate is formed of Au_2S_3 , which, when washed free from acid, dissolves in ammonium sulphhydrate, producing ammonium sulphaurate, whose formation is not attended with any danger. This solution is decomposed by acids, and the gold sulphide again precipitated.

Most of the poisonous vegetable alkaloids, such as strychnia, morphia, nicotine, &c., afford nearly insoluble yellow compounds with gold trichloride; hence the latter is often employed in the search for such bodies as those referred to.

CHAPTER XXXII.

EXPERIMENTS WITH SILVER AND ITS COMPOUNDS.

SILVER, Ag' (*argentum*)=108.—The earlier experiments of our series have made the student acquainted with some of the facts concerning silver and its salts. Thus we found, in the course of Experiment 13, that silver nitrate is completely resolved into pure silver, oxygen, and gaseous oxides of nitrogen by *heat alone*, and that 170 parts of the nitrate can afford 108 of pure silver. We also ascertained that reduction of the nitrate is easily effected by the electrochemical methods pursued in Experiments 14, 15, and 36, while in subsequent experiments we found that silver could afford an insoluble chloride, iodide, bromide, sulphide, antimonide, and many other compounds. Owing to the facility with which most silver compounds undergo reduction, the metal is often found native, like gold and platinum, and in considerable quantity, especially at Kongsberg in Norway, Freiberg in Saxony, and Huantaya and other localities in Peru and in Mexico; but a very large proportion of the metal employed in commerce and in the arts is derived from native compounds of silver, such as 'horn silver,' or the chloride AgCl ; silver-glance, Ag_2S ; arsenio-sulphide and antimonio-sulphide, or light and dark red silver ores, Ag_3AsS_3 and Ag_3SbS

and other analogous bodies, or from argentiferous galena—the sulphide of lead.¹

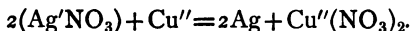
Experiment 431.—Add to some mercury contained in a crucible a fragment of silver derived from the nitrate, as in Experiment 13. The silver dissolves, and an *amalgam* is easily formed, which is liquid if the proportion of silver be small, or solid when the precious metal reaches 16 to 18 per cent. of the amalgam. Just as in the corresponding case with gold, the mercury can be distilled from the amalgam by heat and the silver recovered.

The method of amalgamation is employed in all the chief processes for the extraction of silver from ores, save in the separation of silver from argentiferous lead. The ores are either roasted with common salt to convert sulphuretted silver compounds into chloride or roasted first and then digested with a solution of salt for the same purpose. In either case the product is mechanically mixed with mercury and crude copper sulphate, which latter facilitates the reduction of the silver compounds by the mercury, and the amalgam formed, when filtered from mechanical impurities, is distilled, and the silver left. The metal so obtained is purified from copper and lead by fusion in a current of air, when the impurities oxidise and form a scum of oxides on the surface of the molten material. Successive films of these oxides are removed from time to time until silver only is left.

Experiment 432.—Into a dilute solution of silver *nitrate* plunge a clean strip of copper, or piece of clean

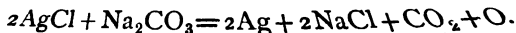
¹ See *Lead* for method of separation of silver by *cupellation*.

copper wire. The copper is quickly coated with a grey deposit of pure silver, which can be removed, washed with water, and dried. This is a convenient mode of reducing silver from its solution.



Experiment 433.—Prepare a small quantity of moist silver chloride by adding common salt or other soluble chloride to solution of silver nitrate, and drain away excess of water; then just cover the silver chloride with dilute sulphuric acid, and place a small strip of zinc in contact with the precipitate, and leave the mixture aside for twenty-four hours. At the end of that time the chloride will be reduced to a grey porous mass of metallic silver, while zinc chloride is in solution. Any excess of metallic zinc remaining can be removed, or dissolved by more acid, and the silver washed and dried.

Experiment 434.—Prepare some more silver chloride and dry it, then mix it with about thrice its weight of 'bread soda,' introduce the mixture into a small clay crucible, and heat the mass very strongly in a fire or furnace with a good draught. When the contents have been in quiet fusion for some time remove the crucible, allow it to cool, and then break it. If the process has been properly conducted a bead of metallic silver can be extracted. In this case the 'bread soda' when heated becomes Na_2CO_3 , and the latter reacts with silver chloride at a high temperature thus—



We may take the silver reduced in this experiment or that obtained by heating the nitrate for our further examination. Silver in its pure state is a fine white metal, of specific gravity 10.56 (water=1). It takes a brilliant polish, but the surface is easily tarnished, especially by gaseous sulphuretted compounds, which form dark-coloured silver sulphide.

The malleability of silver is nearly as great as that of gold, and the metal can be beaten out into very thin films. These 'silver leaves' are sold in books at a small price, and are used in silvering letters, ornamental work, etc. As might be anticipated, silver can be drawn into exceedingly fine wire. Silver is the best conductor for electricity and heat amongst the simple metals.

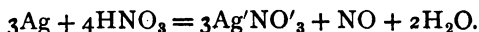
Experiment 435.—Fuse a small fragment of pure silver before the blow-pipe, using a clay support (a piece of broken clay crucible). A very high temperature—well above $1,000^{\circ}$ C.—is required for fusion. When the bead of metal is allowed to cool it often throws up little projections or 'spits' at the moment of solidification. This is due to the fact that molten silver dissolves about twenty times its volume of oxygen gas from the air, but the solid metal cannot retain the oxygen; consequently the gas is evolved with effervescence or bubbling when the metal cools down to a pasty condition. When silver is melted in contact with charcoal the 'spitting' does not occur in cooling, because the carbon combines with and removes the oxygen.

We already know pure silver to be very malleable and 'soft,' but it is rendered comparatively 'hard' and

wear-resisting without material loss of colour by alloying with a small proportion of copper. Advantage is taken of this fact in the production of silver plate, coins, etc. The composition of British silver coinage is—

Silver	92'5
Copper	7'5
	<hr/>
	100'0

Experiment 436.—Digest a small bead of pure silver in a little nitric acid, diluted with about half its volume of water. The metal quickly dissolves, with evolution of ruddy fumes, and the liquid when evaporated nearly to dryness affords colourless crystals of silver nitrate. These crystals dissolve in their own weight of water, and afford a neutral solution; they are also soluble in alcohol. The following reaction takes place during solution of the metal in the acid:—



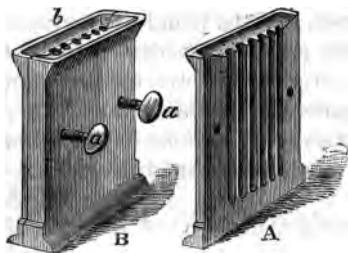
Thus the silver atom acts as a monad in the nitrate.

When the only source of the nitrate is worn-out silver coin, the following method may be adopted in order to get rid of copper. The solution of the metal in nitric acid is diluted with much water, and a solution of common salt added with agitation until no further precipitate of silver chloride is produced. The mixture is then thrown on a filter, and the liquid which passes through contains all the copper. The precipitate of silver chloride is well washed with hot water, then dried, and reduced, as in Experiment

434. The pure silver thus obtained is then dissolved in nitric acid and crystallised.

Experiment 437.—Melt a few crystals of silver nitrate in a narrow glass tube; the salt becomes liquid below a red heat. Then allow the tube and its contents to cool, when the nitrate solidifies, and can be removed, on breaking the tube, as a little rod resembling the sticks of 'lunar caustic' used by surgeons. The sticks are obtained in a similar way, but the molten silver nitrate is poured into cylindrical moulds lined with silver, and then allowed to solidify.

FIG. 121.



The moulds are made in two parts (one half is shown at A, fig. 121), and the two parts are held together by screws *a a* at B. The molten material¹ is poured into the cylinders at *b*, and when the salt solidifies the screws are removed and the parts separated, then the sticks of caustic can be taken out.

We already know, from Experiment 4, that silver nitrate is easily discoloured by light, especially in contact with organic matter, which latter quickly determines its reduction to metallic silver. Thus a drop of the solution allowed to fall on the skin quickly produces a black stain. Silver nitrate is

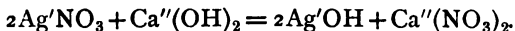
¹ A small proportion of silver chloride is sometimes added to the fused metal in order to render the sticks cast less brittle than when the pure nitrate is employed.

occasionally used for internal administration as a medicine, but it is found that when the doses are continued for a considerable time the skin of the patient assumes a bluish or dusky hue. This discolouration is due to the reduction of the silver salt in the tissue. The nitrate is also used as a *hair dye*, the dark deposit of reduced silver being easily formed on grey hair. A solution of the nitrate thickened with some gum arabic serves as an indelible *marking ink*, as letters written with this ink on cloth or linen quickly become black when exposed to light or when the material is strongly heated.

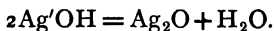
Experiment 438.—Add very dilute solution of ammonium hydrate, drop by drop, to solution of silver nitrate, until the brownish precipitate first formed *just* disappears. The liquid is now a solution of *ammonia-silver nitrate*, $\text{AgNO}_3 \cdot 2\text{NH}_3$. This compound can be crystallised out from the liquid by slow evaporation, but the solution only is frequently required as a test, and the evaporation should not be carried out, as there is a risk of producing an explosive body.

Experiment 439.—Either potassium or sodium hydrate added to silver nitrate causes a brownish precipitate, which does not dissolve in excess as in the last case. The precipitate chiefly consists of silver hydrate, $\text{Ag}'\text{OH}$, but is always mixed with more or less white or yellowish-white *silver carbonate*, $\text{Ag}'_2\text{CO}_3$ derived from the alkaline solutions used, which are rarely free from carbonates. The British Pharmacopœia directs that lime water—solution of calcium hydrate—should be used to precipitate, as that liquid

is certain to be free from carbonate. In this case —



The silver hydrate speedily changes, water and silver oxide resulting, thus—



This decomposition is complete at a temperature of 70° C. The oxide when collected and dried is a nearly black powder, which is easily resolved into silver and oxygen at a temperature but little above that of boiling water. The oxide is easily dissolved by nitric and other acids forming salts. When digested in the ammonium hydrate it forms the dangerous compound *fulminating silver*, which the student should avoid producing, since it is a violent explosive.

A silver peroxide, Ag_2O_2 , is formed on the positive pole during the electrolysis of a solution of silver nitrate. This oxide is not known to form salts with acids.

Experiment 440.—Add sulphuretted-hydrogen water to solution of silver nitrate, when a black precipitate of silver sulphide, Ag_2S , is formed. This body is not soluble in yellow ammonium sulphide, unlike the platinum and gold sulphides. The compound occurs native as *silver glance*.

Experiment 441.—Add to a solution of a soluble silver salt a few drops of hydrochloric acid, or a solution of a metallic chloride, when a white curdy precipitate is formed, which is insoluble in dilute hydrochloric or nitric acids, and soluble in but very small

quantity in the concentrated acids. Silver chloride rapidly changes to a slate-blue colour under the influence of light. The precipitate easily dissolves in ammonium hydrate, and forms the compound $2\text{AgCl}_3\text{NH}_3$, but silver chloride can be reprecipitated from the solution when the ammonia is neutralised by an acid. Perfectly dry silver chloride readily absorbs ammonia gas; one gram of the anhydrous chloride absorbs 325 c.cs. of dry ammonia, and the compound parts with the gas when heated to 37°C . Faraday utilised this compound in the liquefaction of ammonia. For this purpose he placed the body at one end of a stout bent tube, which was then hermetically sealed. On applying heat the ammonia was evolved and condensed under its own pressure in the other end; when the source of heat was removed the liquid ammonia disappeared, being reabsorbed by the silver chloride.

Silver chloride is found native in dark translucent masses termed 'horn silver,' or *cerargyrite*.

Experiment 442.—Repeat Experiment 178, adding solution of potassium iodide to silver nitrate, and note the fact that the pale-yellow silver iodide— AgI —precipitated is insoluble in dilute nitric acid, and is very slightly soluble in ammonia solution. The iodide precipitated from excess of silver nitrate becomes greenish on exposure to light.

Silver iodide is found native in small quantity as *iodyrite*.

Experiment 443.—Repeat Experiment 197, adding solution of potassium bromide to silver nitrate. The nearly-white precipitate of silver bromide— AgBr —

formed is insoluble in dilute nitric acid, and is only slightly soluble in ammonium hydrate, unless the solution of the latter be very strong. The bromide precipitated from excess of silver nitrate becomes of a greyish colour under the influence of light.

Silver bromide is found native as the mineral *bromyrite*.

Silver fluoride— AgF —is also known; it is a very soluble salt, which is easily formed by dissolving silver oxide in hydrofluoric acid.

Experiment 444.—Add a few drops of solution of potassium chromate— KCrO_4 —to neutral silver nitrate, and observe that a fine, deep-red precipitate of silver chromate— AgCrO_4 —is formed, which is easily changed to white silver chloride by addition of hydrochloric acid or a chloride, and which is easily soluble in dilute nitric acid.

Experiment 445.—Prepare some moist silver chloride, as in Experiment 441—and divide in two parts:—

a. Add to this portion sodium thiosulphate solution, the silver chloride rapidly dissolves, and the solution now contains the salt AgNaSO_3S . The iodide and bromide dissolve with a similar result in the thiosulphate. See also Experiment 312.

b. Over the second portion pour solution of potassium cyanide, KCN . Into that solution the chloride quickly enters. The liquid then contains the compound AgCN , KCN . The iodide, bromide, and other salts of silver are easily dissolved, and in a *similar way by thiosulphate and by potassium cyanide solutions.*

The solvents for silver salts above employed are largely used in photography for the purpose of 'fixing,' and the cyanide solution is employed in electroplating, in the same manner as the corresponding gold solution (see p. 73).

In addition to the class of silver salts prepared as just stated, Wöhler obtained another series of compounds from silver citrate, which had been heated to 100° C. in hydrogen. Thus by the action of potash on the reduced citrate he obtained the oxide Ag_4O , and by the action of hydrochloric acid the chloride Ag_2Cl , termed respectively argentous oxide and chloride. We are therefore acquainted with three oxides and two chlorides of the metal, viz. :—

Oxides	.	.	Ag_2O_2 , Ag_2O , Ag_4O .
Chlorides	.	—	AgCl , Ag_2Cl .

It is difficult to explain the constitution of argentous oxide without assuming the silver atom to act as a diad at least, instead of a monad or single link element—and certain relations of crystalline form traceable between some salts of silver and those of the diad metal copper tend to strengthen this conclusion. We shall, however, reserve further remarks on this point until we have made some experiments with copper, but there is no doubt that silver acts in all its ordinary compounds as an apparent monad.

The art of photography depends on the fact that silver compounds, but more especially the chloride, bromide, and iodide of the metal, are either distinctly discoloured under the influence of light—*chiefly that of higher refrangibility*—or are so affected

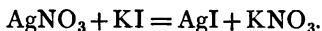
as to be materially changed in their chemical characters and relations, but without visible alteration. The former change takes place very slowly by comparison with the latter effect, which is obtained with great rapidity. The two main operations in photography consist in *taking the negative*, and producing from it a *photographic print*. The following experiments illustrate these prime processes, and also the differences above referred to in the action of light on silver salts.

Experiment 446.—Obtain from any vendor of photographic chemicals a small quantity of iodised collodion—a solution of potassium or other iodide¹ in a mixture of alcohol and ether, which also holds a body resembling gun-cotton, termed pyroxiline, in solution. Pour some of this liquid over a small and clean glass plate; the ethereal solvent soon evaporates and a transparent film is left on the glass, which includes the iodide. Before the film is quite dry bring the glass into a room from which daylight is quite excluded, and lighted only by a candle-flame surrounded by a screen of yellow paper; then lay the glass film side upwards on a dish, and pour into the latter, but not directly on the film, a solution of silver nitrate² so that the liquid may cover the collodion layer. The latter soon changes, losing its trans-

¹ Commonly containing bromides as well.

² Containing about 2 grams of the nitrate in 30 cs. of water. As silver iodide is sensibly soluble in this liquid, add a few drops of *potassium iodide*, agitate and filter. The liquid is thus saturated *with silver iodide*, and therefore cannot dissolve more from the *collodion film*.

parency, and being converted into a translucent, yellowish layer, owing to the formation of silver iodide within the film by double decomposition between the silver nitrate in the 'bath' and the iodide of the collodion. Thus—

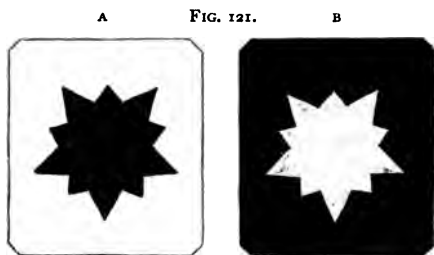


After a few minutes the plate is to be removed from the bath and allowed to drain; it is then termed the 'sensitive plate.'¹ A piece of cardboard, from which some pattern has been cut, is now placed immediately over, but not in actual contact with the moist film, which is now very sensitive to light, the plate so covered is brought to the door of the room, and exposed to diffused light for five to fifteen seconds, according to the brightness of the light, then brought back into the room, and the cardboard removed. On examination in the yellow light of the room no trace of an image of the perforation in the cardboard will be observed, unless the exposure to white light has been much too long. Now place the plate film upwards in a clean dish, and pour over it a solution of ferrous sulphate.² The film should now gradually darken wherever the light has acted upon it, and the image should grow in intensity until the form of the

¹ The use of collodion and a bath is now often dispensed with, and a solution of gelatine holding in mechanical suspension a sensitive silver salt is used at once to coat the glass plate, which is then ready for exposure.

² Containing one gram in 30 c.cs. of water and 1 c.c. of acetic acid. The latter retards and regulates the reducing action of the iron salt.

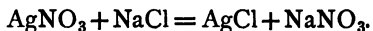
perforation in the cardboard is quite distinct. Hence, though no *visible* change was produced in the first instance by the action of light, a marked *chemical* difference between the exposed and unexposed film appears when acted upon by the ferrous sulphate, which latter is a powerful reducing agent, and is technically termed a 'developer.' The unchanged silver salts in the film are still sensitive to light, and must be removed by immersing the plate in a strong solution of sodium thiosulphate or 'hyposulphite,' which, as in Experiment 445, dissolves the unaltered silver iodide, and so 'fixes' the picture; the film is then washed with



water, and can be brought into the light with safety. The image consists of reduced silver on a clear ground, something like A, fig. 121. This is the *negative*, analogous to that obtained in the photographic camera, whereon the brighter portions of an object are represented by a deposit in the film. The next operation is that of *printing* from the negative on paper.

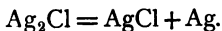
Experiment 447.—Obtain a sheet of plain photographic paper, which has been salted by soaking in a weak solution of any chloride, such as that of sodium or ammonium. Paint over the prepared *side of the paper* a rather strong solution of silver *nitrate in the dark*, and hang up to dry. Chloride of

silver is formed in the paper by double decomposition. Thus—



When the paper is dry the negative is placed film side down on it, and white light allowed to act on the paper through the negative. Gradual discolouration of the paper takes place wherever it is not protected by the deposit on the negative. After sufficient exposure to produce a good deep colour the paper is removed to the dark room, and well soaked in water, and washed to remove all free silver nitrate; it is then 'fixed' by a thiosulphate bath, as in the case of the negative. Before or after fixing the image may be 'toned,' as described under Experiment 429. The *print* then resembles B, fig. 121.

The *visible* change observed during the action of light on the chloride of silver is probably due in great part to the formation of a compound analogous to Wöhler's argentous chloride Ag_2Cl , and this, under the action of the fixing agent, is decomposed thus—



The argentic chloride dissolves in the thiosulphate, leaving the metallic silver to form the shadows of the fixed picture. But even before the action of the fixing agent free silver is present in the darkened portions of the picture, owing to reduction of some of the excess of silver nitrate left in the tissue in the presence of the organic matter of the paper.

CHAPTER XXXIII.

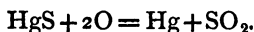
EXPERIMENTS WITH MERCURY AND ITS COMPOUNDS.

MERCURY. Hg'' (*Hydrargyrum*) = 200.—This element resembles the noble metals, as we have seen (Experiment 56), in affording an oxide which is easily reduced at a comparatively low temperature; but, unlike members of the group referred to, the oxide of mercury can be formed by the direct union of its elements. Moreover, Experiments 35 and 36 taught us that mercury is electro-positive to silver, though electro-negative to copper and many other metals not yet examined in detail.

Mercury is met with in the free state, but to a very small extent; its chief mineral compound is the sulphide termed *cinnabar*, HgS . This mineral is dark red in colour, and when well crystallised occurs in rhombohedra. Its specific gravity is 8.998 (water=1). When scratched it affords a rich red streak, sometimes approaching to vermilion in brilliancy—in fact, it is the native form of vermilion.

Experiment 448.—Heat a little powdered cinnabar in a tube similar to that used in roasting *mispickel* (see fig. 113); sulphur dioxide is produced, and droplets of mercury are seen to condense on the sides

of the tube. Cinnabar is, therefore, easily decomposed and reduced by mere roasting in air, and the mercury is converted into vapour in the process. In this case



Experiment 449.—Mix a little of the powdered cinnabar with some quicklime, also in powder; introduce the mixture into a tube closed at one end, and heat. Mercury is driven off, and the vapour condenses on the cool sides of the tube. When examined by a magnifier the appearance is that of fig. 122.

FIG. 122.



The chief cinnabar mines are those of Almaden in Spain and Idria in Austria, though the mineral is very widely diffused, as it also is found in California, Peru, China, and Japan. The reduction of the cinnabar is as simple an operation as the above experiments would lead us to anticipate. The crude ore is roasted in a special furnace, and the gases with vapour of mercury are carried through a series of large brick condensing chambers or through short jointed earthen tubes, the mercury condenses, and the sulphur dioxide and other gases pass away into the atmosphere. In some cases heating with lime or limestone, as in the above experiment, is resorted to, the mixture being heated in large retorts and the mercury distilled over. The crude mercury is filtered through linen, and is then sent into commerce in stout bottles of wrought iron.

Experiment 450.—Introduce some crude mercury

into a small retort, and apply heat. When the temperature reaches 357° C. the mercury boils, and the vapour condenses in the neck of the retort and trickles into a receiver. It is difficult to avoid 'bumping' as the liquid boils, but a steady temperature best secures a regular ebullition. Any impurities, such as lead, zinc, copper, &c., are left in the retort, and the distillate is pure mercury.

The impurities just referred to when present in mercury make a globule 'tail' when allowed to run along a board; this is due to the rapid oxidation of the impurities, whereby a scum of oxide of lead, zinc, &c., is formed, and this interferes with the free movement of the drop which is then drawn out to a pear-shaped form. Distillation is the best mode of purification, though occasional agitation during several days with a solution of mercuric nitrate (see Experiment 456) is also effectual when rapid treatment is not necessary.

Pure mercury obtained by either method is a liquid metal of a bluish-white colour. Its specific gravity is 13.59 (water=1). At -40° mercury becomes a white crystalline and rather brittle solid. Even when solid mercury gives off vapour. The boiling point of the liquid metal is, as already stated, 357° C.

The specific gravity of mercury vapour is 100 (H=1): its atomic weight should therefore be 100, and its molecular weight 200; but the specific gravity of the vapour of the highest chloride of the metal—*mercuric chloride*—is 135.2, hence its molecular weight is 270.4. If from the latter value we subtract the

weight of two atoms of chlorine ($35.5 \times 2 = 71.0$), that of the residue is 199.4, or nearly 200, and less than this is not known to take part in chemical change; hence the atomic weight is 200, and mercury is a diad metal. The specific gravity of mercury vapour is therefore anomalous as the gaseous molecule contains but *one* atom.

The weight of liquid mercury that contains at 100° C. the same quantity of heat as 108 parts of pure silver at the same temperature is 208 parts; thus the heat capacity of mercury also fairly accords with the atomic weight 200.

When globules of mercury are triturated in a mortar with various powders the globules disappear, and the product in each case is a mechanical mixture of the powder employed with very finely-divided mercury almost wholly uncombined, though during trituration slight oxidation occurs. Several mechanical mixtures of this kind are employed in medicine; thus, the well-known *grey powder*, or *hydrargyrum cum creta* B.P., is such a mixture of mercury with chalk; a similar mixture with magnesia is also used. When lard, suet, and mercury are rubbed together until metallic globules cease to be visible, the *blue ointment*, or *unguentum hydrargyri* B.P., is obtained. Again, *blue pill* is a similar mixture of mercury with conserve of roses and liquorice powder, and *mercurial plaster* also contains the free metal.

Mercury dissolves many metals and forms alloys with them, which are specially termed *amalgams*. An amalgam with *sodium* was prepared in Experiment 124, and a *potassium* amalgam can be similarly obtained;

a gold amalgam was produced in Experiment 425, one with silver in Experiment 431, and with tin an amalgam is produced which forms the reflecting back of an ordinary glass mirror (see p. 50).

Plates of metals can be superficially amalgamated; thus a sheet of copper is made to look like silver by rubbing the surface with mercury and dilute sulphuric acid—the latter to remove any film of oxide—while the mercury alloys with the clean metallic surface. In a similar way zinc plates are superficially amalgamated for use in galvanic cells; the plates thus superficially amalgamated possess the advantage of resisting attack by the diluted sulphuric acid of the cells in which they are usually immersed, until the galvanic circuit is completed.

In one of our earliest experiments (Experiment 6) a compound of mercury was formed by triturating in a mortar the metal with iodine. It was then stated that if the proportion of iodine be large the resulting powder is red in colour; if little iodine be employed, the colour is dull green. When the experiment is conducted with care it is found that the red compound is formed when one atom of mercury and two atoms of iodine are made to unite: hence the composition of the product is HgI_2 ; whereas, when one atom of metal and one of iodine are triturated until all the mercury disappears, the green or yellowish-green iodide HgI results.

Experiment 451.—Rub in a mortar 200 c.grs. (one atom of mercury) and 127 c.grs. (one atom) of *iodine*, adding occasionally a few drops of spirit of *wine* in order to facilitate combination for the reason

assigned under Experiment 6. When metallic globules are no longer visible the whole assumes a yellowish-green colour. The product is the *green iodide of mercury*, B.P.

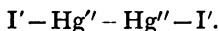
Experiment 452.—Repeat the experiment, but use 254 c.grs. (two atoms) of iodine for 200 c.grs. (one atom) of mercury. A rich red product is obtained when the operation is complete, which is the compound HgI_2 .¹

We have already produced the same body by a different method (in Experiment 180), when potassium iodide was added to solution of mercuric chloride, and it is this latter process that is directed in the 'British Pharmacopœia' for the preparation of the red iodide of mercury. If the moist precipitate of the red iodide be spread thinly over paper and the whole dried rather strongly over a lamp, the compound changes colour and becomes yellow, and remains so on cooling. When the yellow body is cold a scratch is sufficient to make it assume the original red colour. The yellow body is therefore but a molecular modification of the iodide.

There are two iodides of mercury: in one of these—the *red* compound—the mercury atom acts as a diad towards the monad iodine; in the *green* compound mercury is an apparent monad. But it is contrary to experience that a two-link, or diad, element

¹ The two iodides of mercury do not readily afford free iodine on heating with sulphuric acid according to the method described in the Analytical Appendix to Part II., but the addition of a little MnO_2 to the mixture at once secures the separation of iodine.

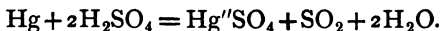
can also act as a real monad. We therefore double the formula of the green salt and write Hg_2I_2 , or



The red compound is generally termed *mercuric* iodide and the green salt *mercurous* iodide, and these bodies are typical of two great groups of mercury compounds.

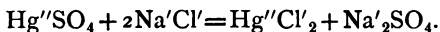
Analogous bromides and chlorides of mercury are easily obtained by direct union of the elements in proper proportion, but the chlorides, which are of chief importance, are bodies which can be easily converted into vapour, and in consequence admit of convenient preparation by the indirect methods we still now carry out.

Experiment 453.—In order to prepare some mercuric chloride, often called *corrosive sublimate*, it is usual to form a sulphate of the metal in the first instance, thus. Heat gently together in a porcelain capsule 20 grams of mercury with 12 cubic centimeters of strong sulphuric acid, stirring constantly until the metal disappears, then continue the heat until a dry white salt remains. This operation should be conducted under a flue, as sulphur dioxide gas and excess of sulphuric acid are driven off. In this process—



In order to prepare mercuric chloride from the product, take 10 grams of the latter, powder very *finely*, and add 8 grams of sodium chloride, also in *fine powder* and enough manganese dioxide to com-

municate a grey colour to the mixture.¹ Introduce the latter into a long and rather wide tube (fully 2 c.ms. diameter), or a small flask, and gently heat over the Bunsen flame. A white sublimate is soon formed on the cool sides of the tube above the heated mixture, and increases in amount until decomposition is complete. The tube is then cut between the residue and sublimate, and the latter removed. The product is HgCl_2 resulting from the double decomposition ²—



This is the method commonly followed on the large scale, and is directed by the B.P.

The mercuric chloride, or corrosive sublimate, so obtained is a crystalline body of high specific gravity, 5.4 (water = 1). It fuses at 265°C . and boils at 295°C . It is soluble in water to the extent of 1 part in 15 of the solvent. It is much more soluble when alkaline chlorides are present or sal ammoniac. It is more soluble in alcohol, and still more so in ether.³ The sublimate is highly poisonous, and must therefore be handled with great care.

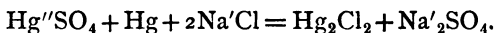
¹ One-tenth of the weights given will suffice for a small operation.

² The office of the manganese dioxide is to liberate a little chlorine from excess of common salt, so as to ensure the conversion of the mercury into the highest chloride. See MANGANESE.

³ Ether, when shaken up with aqueous solution of mercuric chloride, extracts the salt and rises to the surface charged with the compound. Advantage is often taken of this fact in the separation of the chloride from complex mixtures.

Several mercuric oxychlorides exist analogous to the body mentioned under Experiment 152.

Experiment 454.—In order to prepare mercurous chloride, or *calomel*, according to the ‘Pharmacopœia,’ rub together in a mortar the same weights of mercuric sulphate and sodium chloride as in the last experiment, but add 8 grams of mercury, and omit the manganese altogether. When the mercury is thoroughly incorporated with the powders introduce the mixture into a tube or flask, and sublime as before. Calomel requires a low red heat for conversion into vapour, and at ordinary pressure does not fuse first. The sublimate forms a white crystalline crust of specific gravity 7·14, but when it is removed and finely powdered it becomes yellowish. On the large scale the calomel is obtained at once in the form of powder by allowing its vapour to pass into a large chamber, wherein by sudden cooling the salt is precipitated as a fine powder. The chemical change during sublimation is the following:—



Calomel can also be formed by heating together mercury and mercuric chloride.

Warm a little of the powdered calomel with water; it does not seem to dissolve, nor does it really enter into solution, but when freshly prepared it contains a little corrosive sublimate; hence the ‘Pharmacopœia’ directs that the crude product shall be washed with boiling water in order to remove all traces of the *soluble and highly poisonous mercuric chloride*.

Calomel is not soluble in dilute nitric acid, but is

dissolved when the latter is strong, mercuric chloride and nitrate being formed. Strong hydrochloric acid only partially dissolves calomel.¹

As we have found the two chlorides of mercury to be volatile at temperatures below a full red heat, it follows that the specific gravity of each vapour can be taken. As already stated, the result in the case of mercuric chloride is the specific gravity 135.2 ($H=1$) for the vapour; therefore the molecular weight of the compound is 270.4; this corresponds with the formula $Hg''Cl'_2$.

Calomel vapour has the specific gravity 117.6 ($H=1$), which nearly corresponds to the formula $HgCl$, whereas on the theoretic grounds already stated in the case of the corresponding iodide (see p. 95) the formula should be Hg_2Cl_2 . There is little doubt, moreover, that the latter formula is correct, and that the anomalous specific gravity above noted is due to decomposition of the calomel vapour into a mixture of that of mercuric chloride and metallic mercury at temperatures above the condensing point, thus increasing the volume and therefore reducing the specific gravity; though when the temperature is lowered recombination takes place and calomel is re-formed. The term *dissociation* is often applied to the changes of this order.

¹ Neither mercurous nor mercuric chlorides readily afford hydrochloric acid when heated with strong H_2SO_4 in testing for the acid radicle according to the Analytical Appendix to Part II., but chlorine is easily evolved on addition of MnO_2 to the mixture of salt and acid. For the distinction of mercurous from mercuric compounds see pp. 102, 103, and 104.

Nitric acid easily attacks mercury and dissolves the metal; by analogy two nitrates should exist corresponding to the chloride and iodide. We shall now experiment in this direction.

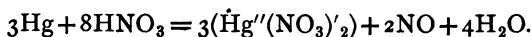
Experiment 455.—Place some mercury in a capsule, and pour upon it nitric acid previously diluted with about four times its volume of water. Action commences in the cold, and when once set up continues until all the metal disappears if a sufficient proportion of acid has been employed. The question now arises whether the solution contains mercurous or mercuric nitrate. We know mercurous chloride to be insoluble in dilute acids, and the mercuric chloride to be soluble; hence, according to Berthollet's first law (Part I. Appendix), hydrochloric acid should precipitate calomel from a mercurous solution, though mercuric nitrate should not precipitate with the same reagent.

Add to a little of the nitrate solution in a test-tube a few drops of hydrochloric acid, and note that a white precipitate is at once formed; this is easily proved to be Hg_2Cl_2 , therefore the solution contains mercurous nitrate $\text{Hg}'_2(\text{NO}_3)_2$.

Allow the strongly acid solution to slowly evaporate in the air, when colourless prismatic crystals will separate, which consist of the above salt with two molecules of water of crystallisation. When the crystals are acted upon by water, a yellow *basic* salt is formed, whose composition is $\text{Hg}_2(\text{NO}_3)'_2, \text{Hg}_2(\text{OH})_2$.

Many other still more basic salts are known—that is *to say, compounds* which contain the normal nitrate *united with more or less metallic hydrate or oxide.*

Experiment 456.—Pour some *strong* nitric acid over a globule of mercury contained in a small porcelain capsule. The acid acts energetically on the metal, and the latter dissolves, while brown fumes are evolved in abundance. Now apply heat, and boil the solution for some minutes ; if necessary, adding a few drops more of nitric acid to secure the complete solution of the mercury. A portion of the liquid when cold is tested with hydrochloric acid, but no precipitate is obtained, therefore the nitrate in solution is mercuric nitrate. When the liquid is evaporated to remove excess of acid fine crystals are formed, and these consist of $2(\text{Hg}''(\text{NO}_3)_2) + \text{H}_2\text{O}$. The reaction is explained by the equation—



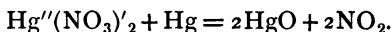
A strong solution of this salt, prepared substantially as above, constitutes the *acid solution of nitrate of mercury*, B.P.¹

Several basic mercuric nitrates are also known.

Experiment 457.—Powder some of the crystals obtained in the last experiment, and when powdered triturate with half the weight of metallic mercury, and heat the mixture gently in a porcelain dish, with constant stirring, until ruddy vapours cease to be evolved, and only an orange-red crystalline powder remains. The composition of this powder is HgO ; it is therefore mercuric oxide—the *red oxide of mer-*

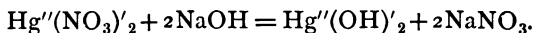
¹ *Millon's reagent* for albuminous and other proteic bodies is a strongly acid solution of the same salt. When added to a solution containing a proteid and heated, a fine purplish-red colour is developed.

cury, B.P., or 'red precipitate' used by surgeons as a local application to certain ulcerated surfaces. It is the product of the following change :—



This oxide dissolves in hydrochloric acid, and forms mercuric chloride. We already know from Experiment 56 that this oxide when strongly heated is easily decomposed into mercury and oxygen. On the other hand, when mercury is heated in air to a temperature well below its boiling-point for some days, it becomes covered with a film consisting of this oxide, and it is in this way that Lavoisier succeeded in separating oxygen from air—the oxide formed then affording the pure gas when treated as in Experiment 56.

Experiment 458.—Add to the solution of mercuric nitrate an excess of caustic soda. Note that a yellow or brownish-yellow precipitate is formed; this consists, in the first instance, of mercuric hydrate—



But the hydrate quickly loses water, and when dried at 100° C. forms a reddish-yellow powder, consisting of the anhydrous oxide in a fine state of division, and in a less dense form than that obtained in the last experiment. It is this precipitated oxide that is required for use in Experiment 152. Mercuric chloride affords a similar product.

When the solution of mercurous nitrate is evaporated to dryness and the residue heated, mercuric oxide results just as in Experiment 457. We cannot, therefore, prepare the oxide analogous to Hg_2Cl_2 n

this way. Hence we try the precipitation method of the last experiment.

Experiment 459.—Add excess of caustic soda to solution of mercurous nitrate, a black or brownish-black precipitate forms. This is washed well and dried; when quite dry it contains Hg_2O , but easily decomposes into $\text{HgO} + \text{Hg}$. The oxide when acted upon by acids reforms the mercurous salts.

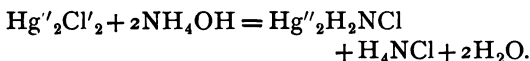
When mercurous chloride is digested with excess of caustic alkali the dark mercurous oxide is also obtained.

The two oxides are produced in the *lotio flava* and *lotio nigra*, B.P.; resulting from the action of lime water— $\text{Ca}''(\text{OH})_2$ —on mercuric chloride, and on mercurous chloride respectively.

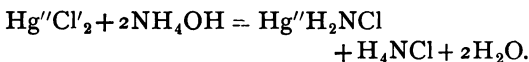
Experiment 460.—Add to a solution of mercuric nitrate or chloride an excess of sodium carbonate solution, a reddish precipitate is at once obtained, the particular colour depending in some degree on the relative proportions of mercury salt and carbonate reacting. But even when the alkaline carbonate is in excess the brown compound precipitated is a more or less basic carbonate, that least basic consisting of $\text{HgCO}_3, 2\text{HgO}$. Mercurous carbonate is pale yellow.

Experiment 461.—Precipitate some calomel from mercurous nitrate, collect the precipitate on a filter, wash the white body with water, and then pour ammonium hydrate over the precipitate on the filter. Blackening at once occurs; this is due to the formation of the dark-coloured compound $\text{Hg}''_2\text{H}'_2\text{NCl}$, which may be viewed as a derivative of ammonium

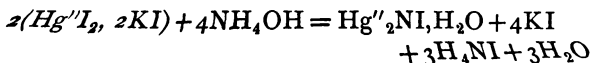
chloride, H_4NCl , half the hydrogen of which latter has been replaced by the diad group Hg''_2 .



Experiment 462. — Add solution of mercuric chloride to excess of ammonium hydrate. Note that a *white* precipitate is formed; this has been found on analysis to contain $\text{Hg}''\text{H}_2\text{NCl}$, and therefore is analogous to the mercurous-ammonium chloride derived from calomel.



This is the *ammoniated mercury*, B.P., often termed 'white precipitate.' Many mercurammonium compounds are known, but the only other body of importance is that produced in *Nessler's* test for ammonia (see note to Experiment 180). The test is an alkaline solution of the compound, HgI_2 , 2KI , and is much used in water analysis. When added to solutions containing very minute traces of ammonia, a brownish-yellow colouration is produced, and the depth of the tint is a measure of the ammonia present; when the proportion of the latter is relatively large a reddish-brown precipitate forms; the composition of this precipitate is given by Nessler as $\text{Hg}''_2\text{NI}, \text{H}_2\text{O}$, resulting from the reaction—



Experiment 463.—Add a little sulphuretted hydrogen water to solution of mercuric chloride or nitrate ; if the latter, the solution must be dilute. Note that a mixture of yellowish precipitate and black particles is first formed, and when the mixture is shaken the precipitate usually becomes a dirty white. The addition of more H_2S changes the colour to dull yellowish, and when enough of the reagent is added to make the liquid smell strongly of the gas, a deep black precipitate is obtained. The latter is mercuric sulphide, HgS .

The colour changes noted are very characteristic, and are due to the formation of successive compounds of mercuric sulphide with the oxide, or with a salt of the metal pre-existing in solution. These compounds are decomposed by excess of sulphuretted hydrogen, HgS resulting. Mercurous sulphide— Hg_2S —is not known.

Experiment 464.—Throw the precipitated HgS on a filter, wash *well*¹ with water, and remove portions, which are to be tested in the following way :—

a. To one portion in a test-tube add moderately-strong nitric acid ; the sulphide does not dissolve even on warming, but the addition of a few drops of hydrochloric acid secures the solution of the black substance. When the excess of acid is evaporated completely, and the residue is dissolved in water, a liquid is obtained, to which confirmatory tests can be

¹ If the precipitate be not thoroughly washed it may dissolve in nitric acid, since any trace of chloride left in it forms nitro-hydrochloric acid, and so dissolves the sulphide.

applied—for example, potassium iodide, as in Experiment 180.

b. Treat another portion with ammonium hydrate and ammonium sulphhydrate. Note that the precipitate does not dissolve. If, however, potassium or sodium sulphides are used instead of the ammonium salt, mercuric sulphide dissolves to a very sensible extent, owing to the formation of a soluble double sulphide, whose formula is, in the case of the potassium compound, $\text{HgS}, \text{K}_2\text{S} + 5\text{H}_2\text{O}$.

The dry mercuric sulphide, when examined under a microscope, is seen to be an amorphous powder, which is velvet black in masses. If a little be heated in a tube closed at one end, from which air is excluded as completely as possible, the sulphide sublimes in *dark red* crystals along with sulphur and some mercury. The crystals afford a fine scarlet powder, identical in *composition* with the amorphous black sulphide; the fine pigment thus obtained is *vermilion*. The latter is, however, generally prepared by triturating mercury and sulphur together and then subliming. The product, after grinding, is washed with potash to dissolve out any uncombined sulphur.

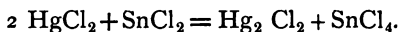
When the sublimed vermilion is obtained in well-defined crystals, it is often found to be almost identical in form with the native sulphide, or *cinnabar*, whose symbol is also HgS .

We have already seen that cinnabar is easily reduced by mere roasting in a current of air and by heating with lime in closed vessels. *All solid mercury compounds* can be reduced by the action of lime, *anhydrous sodium carbonate*, or other alkaline bodies

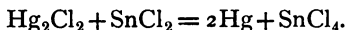
at a high temperature. When the experiment is conducted in a tube closed at one end, droplets of mercury condense on the sides of the tube above the heated mixture, and are then easily identified.

Reduction from solution may be effected either by chemical or electro-chemical action.

Experiment 465.—Add to a solution of a mercuric salt some stannous chloride (*vide* Experiment 404), containing free hydrochloric acid. If the mercury salt be in excess a white precipitate of calomel forms ; thus in the case of mercuric chloride—



If, however, the tin salt be in excess, and particularly if the solutions are near the boiling temperature, any mercuric chloride that may be formed in the first instance is reduced to metallic mercury, thus—



The metal separates as a heavy grey powder, whose particles can be easily made to coalesce by stirring or rubbing together and form globules of the liquid metal. Most other reducing agents can bring about the separation of the metal, especially when aided by heat.

Experiment 466.—Plunge a piece of bright copper wire into an *acid* solution containing mercury. The wire quickly becomes coated with a grey deposit. When withdrawn, dried, and rubbed, the copper is seen to have a bright silvery coating, owing to the superficial formation of an amalgam of copper. The metal can thus withdraw mercury from complex organic

mixtures, just as it does arsenic in Reinsch's test (see Experiment 369), and the mercury can be driven off the copper by heating the coated metal in a tube, when the distilled droplets of quicksilver are easily recognised.

This test is distinctly electro-chemical, but another electro-chemical test can be described, and is easily performed in the following way:—

Experiment 467.—Place a drop of solution of mercuric chloride acidulated with hydrochloric acid upon a clean gold coin. Now touch the latter *through the drop* with an ordinary steel key.¹ The gold will be quickly coated with a silvery layer of mercury wherever touched by the liquid. The coin can be washed and dried without losing the coating, but the latter is easily removed by heat or the action of a drop or two of somewhat diluted nitric acid without injuring the coin.

Poisonous actions.—Pure liquid mercury is apparently non-poisonous, but the frequent inhalation of its vapour leads to the development of symptoms of poisoning. Thus persons engaged in mercury mines or smelting works, mercurial mirror factories, &c., frequently exhibit the most characteristic symptom of slow mercurial poisoning, namely *salivation*—*i.e.*, the profuse flow of saliva from the mouth, accompanied by loss of appetite, trembling and general emaciation. Similar symptoms can be developed by the application of 'blue ointment' to the skin.

Corrosive sublimate, or mercuric chloride, is one of

¹ Iron when alone can separate mercury from its solution, but an amalgam of iron is not formed.

the most poisonous of the compounds of the metal, as about two decigrams (three grains) have destroyed life in the case of a child. This chloride has been frequently administered in mistake for calomel, or mercurous chloride, which latter, owing probably to its slight solubility, is very much less active and is often given in comparatively large doses in the treatment of disease. In ordering the last-named chloride it should always be termed 'calomel,' so as to remove any doubt as to the body intended. In *acute* poisoning by corrosive sublimate there is a strong metallic taste perceived by the patient, burning heat in the throat, and violent pains in the stomach, followed by vomiting, dysenteric symptoms, sometimes convulsions, and death. It is therefore a powerful irritant.

The special *antidote* to be used in poisoning by a soluble mercuric salt such as corrosive sublimate is *albumen* in the soluble form met with in white of egg. The latter should be beaten up with milk and freely administered. Albumen causes a mercurial precipitate with solution of mercuric chloride, and if this occurs in the stomach time is given for the elimination of the poison by vomiting.

CHAPTER XXXIV.

EXPERIMENTS WITH COPPER AND ITS COMPOUNDS.

COPPER. Cu'' (*Cuprum*)=63. We know from previous experiments that copper follows mercury very closely in electro-chemical order, and we shall presently find that it affords some compounds analogous to the mercurial salts already examined.

Metallic copper occurs native in comparatively small quantities, and most of the metal used in the arts is derived from (a) *oxidised* ores, such as the black oxide CuO , ruby or red copper ore, Cu_2O , and *malachite*,¹ which is a basic carbonate often used for ornamental purposes; (b) *sulphuretted* ores, as copper glance, Cu_2S , copper pyrites, Cu_2S , Fe_2S_3 , and bornite, often termed purple or horseflesh copper (Cu_2Fe)S. The metallurgical treatment of the former ores is simple, and is illustrated under Experiment 469, but the smelting of the sulphuretted ores is a complex series of operations, an outline of which will be found at p. 122.

There is no difficulty in obtaining metallic copper in a nearly pure condition, as it is met with in the best wire of the metal. We can also obtain the pure metal from any of its salts by the electro-chemical method described under Experiment 24, *i.e.*, by the

¹ For the composition of this mineral see under Experiment 477.

action of clean iron ¹ on a copper solution, or by the *electrolytic* method described under Experiment 5, which involves the use of a galvanic current, generated outside the liquid in which the copper separates.

Copper is easily seen to possess the metallic characteristics. Its specific gravity is 8.95. The colour of the metal is red ; it is very malleable and ductile, as it can be drawn into very fine wire, and the latter has considerable tenacity. It is an exceptionally good conductor of heat and electricity. It requires a bright red heat approaching to whiteness for fusion. The weight of copper that contains at 100° C. the same quantity of heat as 108 c.grs. of pure silver at the same temperature is 65 c.grs. Copper alloys with several metals ; thus we have already found that it forms with tin *bronze* and *speculum metal*, but its chief alloy is *brass*, 100 parts of which usually contain from 60 to 70 of copper to 40 or 30 of zinc ; the less copper in the material, the lighter is its colour and the greater its hardness. Brass is simply obtained by adding the necessary proportion of zinc to the fused copper ; after sufficient mixture of the molten material it is cast in ingots. *Argentine* is a white alloy of copper, zinc, and nickel, which is much used as a foundation for plating with silver.

Owing to the risk of poisoning attending the use

¹ Copper in solution is most easily detected by plunging a clean knife-blade into the liquid, when the red metal separates. Copper present in mine water is extracted on the same principle, as the water is allowed to flow over scrap iron, when the more valuable metal is deposited, while iron takes its place in solution.

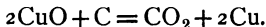
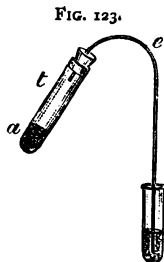
of copper utensils in cooking (see p. 124), these are often tinned internally by heating the surface along with sal ammoniac, and when thus cleansed applying molten tin, which superficially alloys with the copper and protects the latter from chemical action.

Experiment 468.—Heat a strip of copper plate for some time either over a Bunsen gas flame or by thrusting it between the bars of a bright coal fire. In either case the metal changes superficially, losing its metallic appearance, while a dark and dull coating forms upon the surface. When cold the coating can be detached from the plate by a blow, and the scales can be reduced to a grey-black powder. The composition of this body when pure is represented by the formula CuO . This compound is, then, the product of the oxidation of the metal in air. For other modes of producing this body see Experiments 476 and 478. It is worthy of note that copper oxide is not reduced by heat alone, and in this respect is in strong contrast with the oxides of mercury, silver, gold, and platinum. It is, however, one of the most easily reduced of the metallic oxides when in contact at a high temperature with deoxidising bodies, such as hydrogen and carbon, or with compounds containing either of the two elements named¹ other than carbon dioxide and water. We already know (see Experiment 52) how

¹ The ease with which such bodies suffer complete oxidation into carbon dioxide and water under the influence of copper oxide, has led to the extensive employment of the latter in the *analysis of organic bodies*. The oxide used for the purpose is *obtained by strongly heating copper nitrate*. See p. 117.

hydrogen acts on the oxide ; the action of carbon is easily demonstrated thus.

Experiment 469.—Mix copper oxide very intimately with about one-twelfth of its weight of charcoal in fine powder, and introduce the mixture into the small tube of hard glass, *t* (fig. 123), provided with a narrow delivery tube, *e*. Heat the mixture at *a*, and allow the free end of the tube *e* to dip under some lime water in a test-tube. The latter soon becomes turbid, indicating that CO_2 gas is evolved, while the residue after long heating in the tube is distinctly reddish in colour, owing to the copper reduced in the following reaction :—



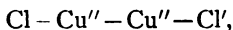
The reduction of the metal from its various oxidised ores is due to a similar reaction, the carbon being supplied by the coal used in the manufacture.

Experiment 470.—Dissolve cupric oxide in somewhat diluted hydrochloric acid until the latter fails to take more up, even on warming the mixture. A rich green-coloured solution is thus obtained, which becomes blue on dilution ; it affords on evaporation crystals whose composition is $\text{Cu}''\text{Cl}'_2, 2\text{H}_2\text{O}$, or hydrated cupric chloride.

When the crystals of the hydrated chloride are heated, water separates and a dark brownish body is

obtained, which consists for the most part of the anhydrous chloride. Metallic copper is scarcely attacked by hydrochloric acid in the absence of air, but the metal easily dissolves in a solution of cupric chloride containing free hydrochloric acid.¹

Experiment 471.—To a strong solution of cupric chloride add some hydrochloric acid, and pour this mixture into a bottle provided with a well-fitting stopper and containing copper turnings. Insert the stopper and let the whole stand for some time. The green or bluish-green colour of the cupric chloride slowly disappears and a colourless liquid is ultimately obtained. If the proportion of hydrochloric acid present be not large, nearly colourless crystals often form on the still undissolved copper, but this crystallisation is prevented if much acid be present. When the solution is added to water a white crystalline body separates, whose empirical formula is CuCl , but since copper acts as a diad in cupric oxide and chloride the formula must be doubled and written $\text{Cu}''_2\text{Cl}'_2$, or



as in the corresponding case of calomel or mercurous chloride. In fact this chloride of copper is termed *cuprous* chloride, and is the type of a class of compounds in which the double atom of copper acts as a diad, like the double atom of mercury in mercurous compounds. The *cupric* chloride produced in Experi-

¹ An oxychloride of copper named *Brunswick green* is obtained by the action of sal-ammoniac solution on copper plates.

ment 470 is the type of a group of bodies analogous to mercuric salts.

Cuprous chloride is slightly soluble in water, though easily dissolved by hydrochloric acid. Its solution in the latter acts as a solvent for carbon monoxide gas, as already pointed out in Experiment 251. Cuprous chloride treated with excess of ammonium hydrate forms a pale blue liquid, which absorbs acetylene gas, as shown in Experiment 261. The solution of cuprous chloride in hydrochloric acid quickly assumes a green or bluish-green colour on mere exposure to the air, as the cuprous chloride passes into cupric chloride thus—

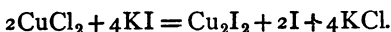


Cuprous chloride ought therefore to act as a powerful reducing agent, and, in fact, it does so act, as we shall find later on.

Bromides and fluorides analogous to the two chlorides are known, but only one iodide of copper is yet known, and that is cuprous iodide.

Experiment 472.—Add to a few drops of a nearly neutral solution of cupric chloride potassium iodide solution in considerable excess, and note that a precipitate forms in a brown liquid. When the mixture is thrown on a filter the brown liquid passes through the paper, and after washing the precipitate on the filter with water it is seen to be a nearly white crystalline powder; this is the iodide $\text{Cu}''_2\text{I}'_2$. Free iodine is easily detected by starch in the brown liquid. Here, then, we meet with a case of reduction from the cupric to cuprous condition without the intervention of

metallic copper, and the following equation represents the change—



Thus an atom of iodine is liberated for each atom of copper precipitated. Iodine is not set free in the operation if the copper solution be mixed with ferrous sulphate previous to precipitation of the iodide.

Experiment 473.—Instead of precipitating with potassium iodide, as in the last experiment, add to the cupric sulphate solution of sodium hypophosphite (see Experiment 347), slightly acidulated with diluted sulphuric acid, and warm the mixture to about 70° C. A brownish precipitate separates, which is another product of reduction and is a cuprous hydride, Cu_2H_2 . If the liquid containing this body be raised to the boiling point hydrogen gas is evolved, and metallic copper remains.

We already know from the result of Experiment 289 that copper dissolves on heating in strong sulphuric acid, with evolution of sulphur dioxide gas and formation of copper sulphate.

Experiment 474.—Repeat this process, and allow the residue to cool ; then throw the contents of the tube into some water. The copper sulphate dissolves and the liquid, when filtered and evaporated, affords fine blue crystals, whose composition is represented by the formula $\text{CuSO}_4, 5\text{H}_2\text{O}$. This is the 'blue vitriol' of commerce ; but much of this salt is obtained on the large scale by carefully roasting *copper pyrites* at a low temperature ; the iron, copper, and sulphur are oxidised, and on digesting the product

with water copper sulphate is dissolved out, as well as iron sulphate, and the solution, when concentrated, affords fine crystals of impure 'blue vitriol.'

Pure crystallised copper sulphate dissolves in about two and a half times its weight of water at mean temperature, and in about half its weight of water at 100° C. When the powdered crystals are dried on a water bath for some time four-fifths of the water of crystallisation is expelled, and a nearly white powder, containing $\text{CuSO}_4, \text{H}_2\text{O}$, is obtained; but if this compound be heated to 240° C. the last molecule of water is removed, and anhydrous copper sulphate remains as 'a yellowish white powder, which becomes blue when moistened with water,' as stated in the 'British Pharmacopœia,' wherein the preparation is directed for use in the detection of water in absolute alcohol by the blueing above noted.

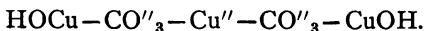
Several basic copper sulphates are known.

Experiment 475.—Place some copper turnings in an evaporating dish and pour over them nitric acid; if the latter be concentrated red fumes of N_2O_3 appear as the metal dissolves; if the acid be rather dilute, colourless NO gas separates which becomes red on mixture with atmospheric oxygen; in each case the metal dissolves and the liquid contains copper nitrate, $\text{Cu}''(\text{NO}_3)'_2$, and when the solution is evaporated blue deliquescent crystals of the salt are obtained.

Experiment 476.—Heat in a small crucible some of the copper nitrate obtained in the last experiment; ruddy fumes are evolved, and when these cease to appear the crucible will contain a dense black powder,

which is pure cupric oxide. The product thus obtained is the form of oxide always used in organic analysis. (See note, p. 112.)

Experiment 477.—Add to a solution of a cupric salt, *e.g.* the sulphate, an excess of sodium carbonate; note that while carbon dioxide gas is evolved, even if the solution were originally nearly neutral, a blue or bluish-green precipitate separates; this when pure is a basic compound,¹ consisting of what may be regarded as the carbonate of a monad group $(\text{CuOH})'$, and may be written $(\text{CuOH})'_2\text{CO}_3$. When dry this body is used for colouring wall-paper instead of the copper arsenite, or Scheele's green (see Experiment 356), and as a general pigment. This carbonate is identical in composition with the mineral *Malachite*. Another mineral carbonate named *Azurite*, in consequence of its fine blue colour, is less basic, and has the composition

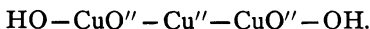


Now boil the mixture containing the precipitate of basic carbonate, and note that the latter becomes black. This change of colour is due to the gradual conversion of the carbonate into a low hydrate of copper.

Experiment 478.—Add to a solution of a cupric salt excess of caustic soda or potash; a bluish precipitate is formed, which is insoluble in excess, and consists of cupric hydrate $\text{Cu}''(\text{OH})'_2$. When the mixture containing this body in suspension is boiled *the precipitate becomes black*, owing, as in the case of

¹ Normal copper carbonate, $\text{Cu}''\text{CO}_3$, is not known.

the carbonate, to the production of a lower hydrate of a brownish-black colour—



When this hydrate is strongly heated it loses all water, and CuO is obtained.

Experiment 479.—Add to solution of *cuprous* chloride either soda or potash in excess; at first a yellow precipitate is produced. This consists chiefly of a cuprous hydrate mixed with a basic chloride; but when the mixture containing the hydrate is boiled the precipitate becomes reddish. The hydrate thus obtained only parts with its water at the temperature of boiling oil, but the cuprous oxide can be easily obtained directly in the following way :—

Experiment 480.—Add some *grape sugar* to a solution of copper sulphate, and then caustic soda or potash until the liquid is strongly alkaline. If sufficient sugar has been added, the cupric hydrate first precipitated by the alkali will dissolve in excess,¹ and form a fine blue liquid. If complete solution is not effected more grape sugar must be added. Now raise the temperature and boil for some minutes; during this treatment a fine red body separates, which is cuprous oxide, Cu_2O , and when the mixture is allowed to stand the oxide subsides easily, leaving a yellowish liquid free from copper. In this case the grape sugar acts as a reducing agent.² The red cuprous oxide is

¹ Many other *organic* bodies enable the hydrate to dissolve in excess of alkali. This is a point of considerable analytical importance.

² Ordinary cane sugar does not afford the reaction, but the

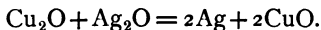
seen under the microscope to be distinctly crystalline, and is identical with the native *red*, or *ruby copper ore*, an impure variety of which is often termed *tile ore*, in consequence of its brick or tile red colour. Cuprous oxide when strongly heated in air takes up oxygen and becomes cupric oxide. When digested with hydrochloric acid it forms cuprous chloride, but with other acids, *e.g.*, sulphuric, it forms cupric salts, and leaves metallic copper. A still lower oxide, Cu_4O , has been obtained by the action of stannous hydrate in alkaline solution on cupric hydrate. This oxide is analogous to that of silver, Ag_4O , already referred to, and partly in consequence of the existence of these analogous oxides it has been suggested that silver (see p. 85) is really a diad metal, and that the best known silver derivatives are analogues of the cuprous compounds, hence that silver chloride should be written Ag_2Cl_2 rather than AgCl . The isomorphism of some silver and cuprous compounds tends rather in favour of this view. A fourth oxide of copper, CuO_2 , has also been obtained, but little is known about it.

Experiment 481.—Instead of adding sodium or potassium hydrate to copper sulphate now add ammonium hydrate, and note that a bluish precipitate is first formed, but this disappears on continuing the addition of the reagent, and a beautiful purple-blue solution is obtained. This is the solution of ammonia-copper sulphate employed in Experiment 356 in the production of *Scheele's green*, or *copper and*

variety of sugar met with in the urine of diabetic patients easily *reduces copper oxide* in alkaline solution, hence the reaction *serves as a test for this kind of sugar*.

hydrogen arsenite. The body formed in solution is $\text{CuSO}_4 \cdot 4\text{NH}_3$. Many other cupric salts afford analogous ammoniacal compounds, and cuprous chloride acts in a similar way with ammonia, but the liquid formed by resolution of cuprous hydrate by ammonia is colourless. The latter is the liquid that we have already used as a test for acetylene (Experiment 261). This solution ought to act as a powerful reducing agent, and we shall now endeavour to make it reduce silver.

Experiment 482.—Prepare some solution of ammonia-cuprous chloride by the addition of excess of ammonium hydrate to cuprous chloride solution, now add to the liquid some ammonia-silver nitrate, and note that a precipitate of metallic silver quickly separates. Silver chloride dissolved in ammonia can be reduced in the same way. The explanation of the reduction is easy, for in any case the ammoniacal liquids used may be regarded as solutions of cuprous and silver oxides which react thus—



The cupric oxide resulting is retained in solution by the ammonia, and the mixture assumes a blue colour.¹

Experiment 483.—Add to ammonia-cupric sulphate a few drops of solution of potassium ferrocyanide, $\text{K}'_4\text{Fe}(\text{CN})_6$, and note that a mahogany-brown precipitate of cupric ferrocyanide, $\text{Cu}''_2\text{Fe}(\text{CN})_6$, is formed as readily as if the solution did not contain ammonia.

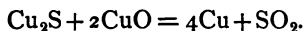
¹ Both cupric and cuprous oxides easily dissolve in ammonium hydrate.

Experiment 484.—Pass sulphuretted hydrogen gas through a solution of cupric sulphate ; a brownish-black precipitate is formed which is insoluble in dilute acids and alkalis, and consists of CuS . This body is *slightly soluble* in ammonium sulphhydrate, but is not dissolved by sodium sulphhydrate. The sulphide is easily dissolved by moderately strong nitric acid. When cupric sulphide is dry, and is heated out of contact with the air, it affords sulphur and cuprous sulphide, Cu_2S .

Cupric sulphide is identical with the beautiful mineral *covellite* or *indigo copper*—so called from its rich indigo blue colour. Cuprous sulphide is met with in nature as *copper glance*, a highly important source of metallic copper. In fact, as already stated, the principal sulphuretted ores of copper worked on an extensive scale are copper glance and copper pyrites, Cu_2S , Fe_2S_3 . The metallurgical treatment of the latter may be thus stated in outline.

The ore is crushed and ‘dressed,’ *i.e.*, separated as much as possible from worthless rock material ; it is then roasted, when much of the sulphur is burnt off as SO_2 gas (along with arsenic), and of the residue the iron chiefly is oxidised. The roasted ore is then fused along with some coal and lime or other suitable ‘flux’ for the earthy impurities, but in all cases silica must be present, since much of the iron is removed in the ‘slag’ as iron silicate, along with the easily fusible calcium silicate; sulphide of copper containing but little iron collects at the bottom of the furnace, owing to its high specific gravity. This product is termed *coarse metal*.

The coarse metal is now roasted to secure the oxidation of the rest of the iron, and the roasted product is again fused, when a very rich sulphide of copper is obtained free from earthy impurities and iron ; this is termed *fine* metal. The fine metal is roasted in turn, when a portion of its copper sulphide is converted into copper oxide and sulphur dioxide gas. On fusing this calcined product, still containing copper sulphide, the metal is at last obtained, and results from a decomposition of the following kind:—



The product is ‘blister copper,’ so-called because the surface is raised in parts and porous, owing to the escape of sulphur dioxide gas while the metal is in a pasty condition. The metal still contains impurities which must be removed by oxidation: for this purpose the cakes of copper are so placed in a furnace that they can be heated in a current of air at a temperature short of the melting point of the metal ; after roasting for some hours in this way the residual sulphur and arsenic, as well as iron, lead, &c., are oxidised, the temperature is then raised to the melting point, and the impurities rise to the surface of the melted copper and are removed. When the process is properly carried out, the copper now contains some cuprous oxide in solution. If this were all allowed to remain the metal when solid would prove brittle ; in order to avoid this, and render the metal tough and malleable, charcoal is thrown over the surface of the copper, and the latter is stirred with a green wood pole, the charcoal and wood soon deoxidise the copper, and it may then

be cast as *tough* copper. The process of *poleing* must not be carried too far, as a minute proportion of cuprous oxide is better left in the copper, since it tends to counteract the injurious effects of traces of foreign metals inevitably present even in the best specimens.

Cases of poisoning by copper salts are not rare owing to the use of copper vessels in cooking, &c. There is no danger when such utensils are kept in a perfectly clean condition, but if vegetable or fruit juices are allowed to stand in them for some time, when exposed to the air, a greenish material termed *vert-de-gris*—a basic acetate of the metal—is formed, and when mixed with food and eaten can set up symptoms of poisoning. Pickles prepared in copper vessels are particularly liable to contamination with the metal.

Copper acts as a powerful irritant, causing colic, vomiting of greenish matter (accompanied by a metallic taste), collapse and death. The symptoms of chronic poisoning are not characteristic, as they consist in general depression, loss of appetite and condition.

The *antidote* commonly recommended in acute poisoning is iron in the form of filings, or as *fer réduit*, the object being to separate the metal as in Experiment 34, but a far safer antidote is *white of egg* beaten up with warm water, as the albumen of egg combines with and precipitates the copper, and then gives time for the elimination of the poison, either by the natural emesis set up by the first action of the irritant or by the use of the stomach-pump. As in *most other cases of irritant poisoning*, the nervous *depression must be met by warmth and stimulants.*

Simple Test for Dissolved Copper. 125

The presence of copper in any suspected articles can be promptly detected on plunging a clean knife-blade into the solution containing some dilute hydrochloric acid, when the well-known reddish stain of metallic copper is obtained after some time, even if no more than mere traces are present.

CHAPTER XXXV.

EXPERIMENTS WITH LEAD AND ITS COMPOUNDS.

LEAD. Pb^{iv} . (*Plumbum*) = 207.—This metal is the next subject of study, as indicated by its position in the electro-chemical series given under Experiment 37, for it can displace copper from its solutions, especially when they are acidulated with acetic acid and heated, while we already know, from the result of the experiment just cited, that zinc, and we may add iron, easily displace lead from its compounds.

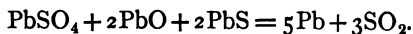
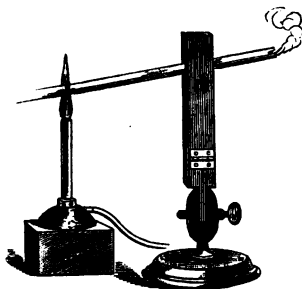
The chief source of lead in nature is the mineral *galena*, or lead sulphide, $\text{Pb}^{\text{II}}\text{S}$, which latter resembles metallic lead very closely in colour. Another, though a comparatively unimportant source of the metal, is the carbonate named *cerussite*, or *white lead ore*, $\text{Pb}^{\text{II}}\text{CO}_3$, while the metal itself is said to have been met with in nature in very small quantity.

Experiment 485.—Heat a little powdered *galena* in a roasting-tube (fig. 124). Care must be taken that the mineral does not melt at first. On roasting for some time the powder changes in appearance, and sulphur-dioxide gas escapes. The roasted residue in the tube contains lead sulphate, PbSO_4 , lead oxide, PbO , and some unchanged sulphide, PbS .

The process carried out in the tube represents the first stage in the metallurgical treatment of galena,

save that a 'flux' is added in order to facilitate the removal of earthy and other impurities. The *second* stage cannot be so easily carried out on the small scale, but it consists in melting the residue of roasting, when metallic lead and sulphur-dioxide gas result from the following reactions between the constituents of the roasted ore—

FIG. 124.



The metallic product is cast into ingots, or *pigs*, of crude lead.

Most specimens of galena contain some arsenic, and such ores when roasting give off fumes of As_2O_3 , which, together with oxides of lead and other metals, are carried along in the current of hot gas, and would, if allowed to pass into the air of the district, soon destroy vegetation and animal life within a comparatively wide radius of the smelting works. In order to avoid these evils, and at the same time to recover valuable material, a very long flue is provided, often over a quarter of a mile in length, through which the fumes have to pass, and in which they condense, while the bodies which are permanently gaseous at ordinary temperature alone escape into the atmosphere.

When the crude lead contains much antimony it

is rendered hard and brittle, so that the 'pig' is easily chipped by blows of a hammer. Such lead is unsuitable for most purposes, save for the production of type-metal or other alloys of lead and antimony,¹ and the latter must be removed. This is easily accomplished by melting the metal and exposing the surface to oxidation. The antimony oxidises much more rapidly than the lead, and a scum is formed which is removed by the workman from time to time until a sample of the metal when allowed to cool exhibits the high malleability of pure lead.

Most samples of crude lead contain silver and traces of gold, which can be profitably extracted. The process most commonly adopted for the purpose is one termed Pattinson's method,² and depends upon the fact that a rich alloy of silver and lead has a lower fusing point than pure lead; consequently in a molten mixture the latter becomes solid at a much higher temperature than the alloy with the precious metal. In practice several tons of argentiferous lead are melted and then allowed to cool. On stirring crystalline masses of pure lead separate, and are removed by means of a sieve-like ladle until about three-fourths of the original quantity has thus been withdrawn; the de-silverised lead is then melted and

¹ See p. 27.

² In some works the silver is removed by throwing zinc into the molten lead; the zinc alloys with the silver but not with the lead, and as the alloy floats on the surface of the metal it can be skimmed off. The zinc-silver alloy is then either distilled to separate the volatile zinc, or digested with diluted sulphuric acid, when the zinc dissolves and silver is left. This is termed *Parkes's process*.

cast for use in the arts. The residue, rich in silver, is mixed with similar products of other operations, and the process of lead extraction continued until a very rich alloy is obtained, from which no more lead can be removed by crystallisation without loss of silver. This point is reached when the alloy contains more than 10 per cent. of silver.

We know already that silver does not oxidise when heated in air, whereas the oxidation of lead is easily effected by the same treatment. Advantage is taken of this fact in order to secure the complete removal of lead from silver. The process consists in melting the rich alloy on a rather porous dish made of bone-ash, and termed a *cupel*. The lead oxidises and forms a scum, which is either blown off the molten metal by a hot air-blast or is partly skimmed off and partly absorbed by the porous cupel. The oxidation proceeds until the last trace of lead is removed, and only a button of silver is left, which then exhibits on cooling the appearance noted under Experiment 435. The silver thus obtained contains any gold originally present in the lead. The two metals can be separated by boiling with sulphuric acid, which dissolves the silver and leaves the gold. The first process is termed *cupellation*, and when carried out on the large scale involves the atmospheric oxidation of large quantities of lead. The product of oxidation of the lead at a high temperature in a strong air current is the compound PbO , which fuses and solidifies on cooling to a brownish scaly body, termed in commerce *litharge*. The process of cupellation is often carried out on the small scale in order to determine the proportion of

silver in a sample of crude lead. For this purpose a weighed quantity of the alloy is placed on a bone-ash cupel of the form shown in fig. 125. The cupel is then placed on the floor of a *muffle* of fireclay (see fig. 126), the closed end and sides of which are heated either in a good coke or gas furnace; but the mouth *m* of the muffle is not enclosed by fuel, so that the process in progress can be watched. The alloy soon melts on the cupel, and oxidation of the lead and other metals, save silver and gold, proceeds in the current of hot air. The oxides formed sink into the porous cupel, and as the last traces of lead leave the

FIG. 125.



FIG. 126.



silver a beautiful play of colours is observed on the surface of the button; when this disappears a brilliant bead of silver remains, which when cold is removed from the cupel and weighed. When the silver bead is dissolved by nitric acid, a small quantity of a brownish powder is usually left; this is *gold*, which can be thus separated from the silver and its weight ascertained.

Experiment 486.—A small quantity of pure lead can be thus prepared. Dissolve crystals of the pure acetate, or ‘sugar of lead,’ in water, acidulate the solution with acetic acid, and suspend in the liquid a strip of pure zinc. A lead-tree (see Experiment 37) is soon formed, and when the zinc has completely *disappeared* the precipitated lead is collected, washed

frequently with water and dried ; it can then be fused to a button in a porcelain crucible. For ordinary purposes good sheet lead, which dissolves completely in nitric acid,¹ may be used instead of the pure metal. Lead is of a bluish-grey colour, and its fresh surface exhibits a fine lustre, but it quickly tarnishes in air. The metal is very soft and malleable, but its ductility and tenacity are low. The specific gravity of the lead is 11.3 (water = 1). It melts at 330° C. ; at a full red heat it is slightly volatile. Lead is largely used in the arts for a great variety of purposes, owing to the ease with which it can be worked and joined, and its comparatively slight tendency to atmospheric oxidation or alteration by acids ; thus in the form of sheet lead it is used for the protection of specially exposed parts of roofs, for the construction of water cisterns, and of sulphuric acid chambers (see under Experiment 303), and as leaden tubing for gas and water carriage. Numerous *alloys* of lead are also employed, from that containing a small proportion of arsenic used in the production of shot² to those richer in other metals, as type-metal (see p. 27), fusible metal (p. 39), pewter and plumber's solder (see p. 50).

Lead is easily attacked and dissolved by nitric acid, but is very slightly acted upon by strong hydrochloric acid or by sulphuric acid, unless the specific gravity of the latter exceeds 1.6. Sulphuric acid of

¹ Indicating absence of tin. The acid used should be diluted and heat applied, as lead nitrate is only slightly soluble in strong nitric acid.

² About six parts per 1,000, added to harden the metal and to facilitate the formation of spherical globules.

higher gravity acts so sensibly on the metal, with production of lead sulphate, that sulphuric acid manufacturers cannot directly prepare a more concentrated acid than 1·6 sp. gr. in the leaden chamber. When the sulphuric solution of the metal is diluted with water lead sulphate separates.

The extensive use of lead in the storage and carriage of potable water, and the known poisonous action of the metal on man, has led to very careful inquiry as to the extent of the possible contamination of water transmitted by vessels or tubes of lead, and the general results of the best experiments made up to the present time may be thus stated :—

1. Pure distilled water, quite free from dissolved air and carbon dioxide, is without any action on lead.

2. Distilled or rain water, containing dissolved air and carbon dioxide, act on lead and form a basic carbonate of the metal, which is mechanically diffused through the water, but is not dissolved unless carbon dioxide be in excess.

3. Ammoniacal salts, but especially ammonium nitrate, according to Muir, as well as nitrites, increase the action referred to under 2.

4. Water containing calcium carbonate, sulphate, phosphate or chloride, *i.e.* 'hard' water, attacks lead at first, but the action soon ceases, possibly owing to the formation of a protective layer on the surface of the metal.

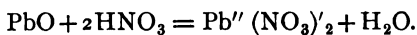
5. Impure lead, particularly that containing antimony, according to Bischof, is more easily attacked than pure lead.¹

¹ A lead-tin alloy containing 3 per cent. of the latter has the reputation of being less easily attacked by a soft water than pure lead.

Generally, then, pure leaden cisterns and pipes can be used with greater safety for a 'hard' water supply than for one that is soft.

The grey film that forms on a surface of lead when exposed to the air at ordinary temperature is an oxide of the metal, whose composition is doubtful owing to the difficulty experienced in separating it from metallic lead. No such doubt exists in the case of the oxide produced at a high temperature, for it is the perfectly well defined compound PbO , and is, as already pointed out; produced under the name of litharge in large quantities during the process of cupellation. We shall begin our series of experiments with this oxide, as it is one of the most easily obtained compounds of lead.

Experiment 487.—Introduce some litharge into a test-tube, and, having noted the appearance of the heavy crystalline scales of the oxide, pour in diluted nitric acid, and heat.¹ The litharge gradually and completely dissolves if sufficient acid be present. Now pour the liquid into a capsule and evaporate until crystals appear, then allow the liquid to cool, when white octahedral crystals of lead nitrate will separate. The crystals are anhydrous.



The same compound is produced when metallic lead is dissolved in nitric acid.

This nitrate is the compound we have already

¹ Litharge is not only used in the British Pharmacopœia for the preparation of lead nitrate as above, but is employed in the preparation of the basic acetate, *q. v.*, and of *Emplastrum Plumbi*—a species of lead soap.

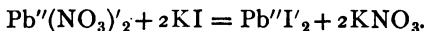
used in Experiment 105 as a source of nitrogen peroxide, *q. v.*

Experiment 488.—Add hydrochloric acid to solution of lead nitrate, and note that a white precipitate is obtained. The white body is lead chloride, and has the composition represented by the formula $Pb''Cl_2$, hence lead is a diad metal at least. If the liquid containing the precipitate be boiled and filtered while hot, the filtered liquid deposits on cooling fine crystals of the chloride, for the latter, though comparatively little soluble in cold liquids, dissolves in thirty parts of boiling water. When water holds less than $\frac{1}{150}$ th of its weight of lead salt in solution at ordinary temperature, it fails to give a precipitate with hydrochloric acid in the cold.

When ammonium hydrate is poured over the precipitated lead chloride it does not undergo any apparent change, and is thus easily distinguished from silver and mercurous chlorides, *q. v.*, but a more or less basic oxychloride is, in fact, formed. Several oxychlorides are known, two of which are met with in nature as the minerals *matlockite* $PbCl_2, PbO$, and *mendipite* $PbCl_2, 2PbO$. Another oxychloride is artificially formed by fusing together lead chloride and oxide in proportions which approximate to the formula $PbCl_2, 6PbO$. The product is yellow, and known as Turner's, or Cassel, yellow. A white hydroxychloride, often termed Pattinson's white, is used as a pigment, and is obtained by adding sufficient milk of lime to lead chloride to replace half its chlorine, and form $Cl' - Pb'' - OH'$.

Experiment 489.—Add potassium iodide solution

to lead nitrate. Note that a fine yellow precipitate separates ; this is lead iodide, PbI_2 , thus produced—



The iodide, like the chloride, is soluble in boiling water, and crystallises out on cooling in beautiful golden spangles. The precipitated iodide is that directed for use by the British Pharmacopœia.

Lead bromide is a white compound easily produced by precipitating lead nitrate with potassium bromide. The fluoride is also obtained as a white precipitate by adding potassium fluoride to lead nitrate solution.

Experiment 490.—Add dilute sulphuric acid to solution of lead nitrate, and note that a white precipitate is formed. This is lead sulphate, $\text{Pb}''\text{SO}_4$, a body which is quite insoluble in diluted sulphuric acid, though it dissolves to a sensible extent in the concentrated acid ; it is quite insoluble in alcohol, and is almost insoluble in pure water, though somewhat soluble if nitric or hydrochloric acid be added. It is easily dissolved by ammonium acetate or tartrate and by strong sodium sulphate solutions.

Lead sulphate is met with in nature as the mineral *anglesite*.

Experiment 491.—Add solution of potassium chromate to lead nitrate, and note that a yellow precipitate forms ; this is lead chromate, $\text{Pb}''\text{CrO}_4$, commonly known as *chrome yellow*, and used as a fine pigment.

We have hitherto dealt only with lead nitrate solution, but the reactions just obtained can be pro-

duced in the solution of any soluble salt of lead, as, for instance, in that of the compound we shall next prepare.

Experiment 492.—Digest in a test-tube some powdered litharge with moderately strong *acetic acid*. Solution is gradually effected, and a liquid is obtained which possesses a sweetish but astringent taste, and affords on evaporation a mass of small crystals. If the solution evaporated had a distinctly acid reaction the crystals consist of hydrated lead acetate, $\text{Pb}''(\text{C}_2\text{H}_3\text{O}_2)'_2 + 3\text{H}_2\text{O}$. This compound is the poisonous 'sugar of lead' of commerce. The crystals effloresce, as they easily part with a portion of their water of crystallisation on mere exposure to the air. The salt dissolves in less than twice its weight of cold water, and in half its weight of boiling water.

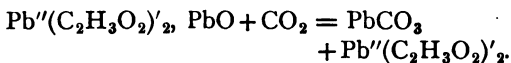
The solution of the salt possesses the power of dissolving lead oxide.

Experiment 493.—Dissolve in a flask ten grams of lead acetate in 50 c.c.s of water, then add seven grams of finely powdered litharge; boil the mixture and keep it at the boiling temperature until most of the litharge disappears, then filter. The solution is colourless, has an alkaline reaction and a sweet astringent taste. It can easily afford the compound $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{PbO}$, a basic or 'subacetate of lead,' as it is termed in the British Pharmacopœia. The constitution of the body may be thus represented—



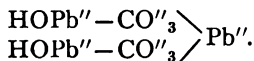
using the symbol Ac' for the acetic group. The solution just produced is often termed *Goulard's extract*.

When the solution is exposed to the air it quickly becomes turbid, and the turbidity gradually increases until a considerable white deposit is formed, which effervesces with acetic acid, and is easily shown to be lead carbonate, or 'white lead.' If a current of carbon dioxide gas be passed through the solution all the lead oxide previously dissolved is precipitated in the form of carbonate, while the original weight of normal acetate is left, thus—



The normal acetate can then be used to dissolve a fresh quantity of oxide for another precipitation by carbon dioxide, and so the process becomes theoretically 'continuous.' This method is now applied on the large scale to the manufacture of white lead for use as a pigment.

Although the carbonate, PbCO_3 , is assumed to be produced in the above process, the dried precipitate contains less carbon dioxide than is required by the formula, and approaches to



The old, or Dutch, process for manufacturing white-lead consisted in exposing rolls of sheet lead to the vapours arising from vinegar and to the gases (consisting chiefly of carbon dioxide) evolved during the fermentation of spent tan or dung, or a mixture of the two. Basic acetate is formed in the first instance, and

then decomposed as above by the carbon dioxide ; the white lead is removed from the plates, washed and ground for use. The covering power of the white lead thus obtained is still superior to that of the product by the first method.

Experiment 494.—Add sodium carbonate solution to lead acetate or nitrate ; note that a white precipitate is produced, which is lead carbonate. The normal carbonate, PbCO_3 , is met with well crystallised as the mineral *cerussite*.

The carbonate is also found in nature combined with lead sulphate as *lanarkite*, $\text{PbCO}_3 + \text{PbSO}_4$; and another compound, $\text{PbSO}_4 + 3\text{PbCO}_3$ is found in two distinct crystalline forms—in rhombohedra, when it is named *susannite*, and in rhombic prisms it is known as *leadhillite*.

Experiment 495.—Heat some ‘white lead’ in a porcelain crucible, and note that moisture is first evolved, but soon carbon dioxide is given off, and the powder becomes yellow. The whole of the carbon dioxide can thus be expelled, and a portion when removed and treated with dilute nitric acid should effervesce but slightly. When this point is reached, PbO remains, but in a more finely divided form than we have met with it in litharge.

The corresponding hydrate is precipitated from soluble lead salts by sodium, potassium, and ammonium hydrate ; the precipitate is soluble in an excess of the two former,¹ but is not dissolved by ammonium hydrate.

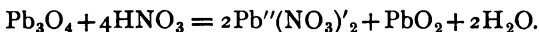
¹ *The resolution is most easily effected in presence of tartaric acid, and allied organic acids.*

Experiment 496.—Again heat the yellow oxide of lead obtained from the carbonate but to a very dull red heat, and stir frequently; by the continued action of heat and exposure to air the oxide deepens in tint, and when allowed to cool is found to have acquired a reddish colour. If the heating be sufficiently prolonged, a red powder is ultimately obtained. This is 'red lead,' or minium, which is produced on the large scale in a precisely similar manner to that just adopted. The composition of ordinary red lead is Pb_3O_4 . It is largely used as a paint for iron, and is employed in the manufacture of flint glass, which latter contains lead silicate, resulting from the action of silica on the red lead added in course of manufacture. The advantage arising from the use of red lead rather than litharge is that the excess of oxygen in the former serves to oxidise carbonaceous matter in the molten glass.

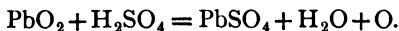
A sesquioxide of the metal, Pb_2O_3 , is also known, but this is not the highest oxide of lead, as we shall now find.

Experiment 497.—Introduce some red lead into a flask, and pour over it diluted nitric acid (about one part of acid to five of water). Agitate the mixture and gently warm. Note that the oxide changes to a brownish colour. After digestion for some time dilute the mixture with water and throw the whole on a filter. The liquid that passes through the filter can be easily shown to hold much lead in solution, by the addition to a portion of it of sodium carbonate in excess, which throws down lead carbonate. The *solid caught* on the filter is to be washed with water

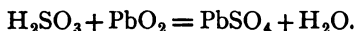
and dried, when it appears as a brown powder, the composition of which is represented by the formula PbO_2 . Hence the action of dilute nitric acid on red lead is thus represented—



The body thus produced is termed *lead peroxide*, as it is the highest known oxide of the metal.¹ When heated with sulphuric acid it affords white lead sulphate and oxygen, thus—



And if treated with sulphurous acid it affords lead sulphate at once, thus—



Thus the peroxide does not act as a basic oxide,² but affords with acids ordinary lead salts, with evolution of oxygen, or proves a direct and powerful oxidising agent; it is often employed in the latter capacity.

Lead peroxide when fused with potassium hydrate forms the compound K_2PbO_3 corresponding to a very feeble acid H_2PbO_3 , of which PbO_2 thus acts as the anhydride. It is probable that red lead is a salt of this acid or a plumbate of lead. Although it is possible to explain the constitution of lead peroxide and

¹ Peroxide of lead can be produced in other ways, notably by the action of a galvanic current on a solution of the metal, when the hydrated peroxide separates at the positive pole.

² It is true that peroxide dissolves in glacial acetic acid, and in strong phosphoric acid, and produces powerful oxidising solutions, but it is doubtful whether these liquids contain true salts.

its related acid without assuming lead to be more than a diad element, it is more probable that it acts in these compounds as a feeble tetrad, since organic chemistry provides us with strong evidence of the tetratomic character of the metal in showing that the lead atom can unite with four monad alcohol radicles.

Experiment 498. — Pass sulphuretted hydrogen through a solution of lead acetate or nitrate ;¹ a black precipitate speedily forms, which consists of PbS. This precipitate is identical in composition with the native sulphide *galena*, but the former is amorphous, while the latter is crystallised in cubes or octahedra.

Lead sulphide is insoluble in dilute acids in the cold, in ammonia and yellow sulphide of ammonium. It is easily attacked by nitric acid even if somewhat dilute, and affords more or less lead sulphate, and nitrate of the metal which passes into solution.

Before leaving the chemical study of lead it is important to note that we have not met with compounds of the metal analogous to mercurous or cuprous salts, most of the lead compounds prepared corresponding in composition rather to the mercuric and cupric salts. On the other hand, in the sesquioxide, red lead and peroxide of the metal, we have types of higher oxides which are either neutral, or feebly acidic in character.

Poisonous effects of lead.—Most of the compounds of the metal are poisonous, especially the soluble salts. The symptoms of acute poisoning are those of a

¹ If hydrochloric acid be present in small quantity, a dull orange-coloured precipitate is sometimes produced at first, not unlike antimony sulphide ; this is a sulpho-chloride of lead.

powerful irritant. Thus 'sugar of lead'—the compound which has most commonly endangered life—causes nausea and vomiting accompanied by violent pains in the abdomen, collapse, and even death after a few hours.

The best chemical antidote is a soluble sulphate, and magnesium sulphate or 'Epsom salts' is that generally preferred; this should be administered in quantities of ten grams at a time dissolved in thin gruel, the aim of this treatment being, of course, to produce the insoluble lead sulphate, and arrest the absorption of the poisonous metal.

Slow or chronic lead poisoning is very common amongst those employed in lead works, and painters. One of the principal symptoms is violent abdominal pain which is often termed 'painters' colic.' This is accompanied by much nervous prostration, and by more or less marked paralysis of the extensor muscles of the forearm. In persons so affected a blue line is commonly observed at the edges of the gums. The treatment consists in the use of drinks containing diluted sulphuric acid, the relief of colic by small doses of sedatives, and baths, while the nervous tone is improved by generous diet, and the use of electricity. It is to be observed that the continued use of water impregnated with small quantities of lead has often given rise to chronic poisoning, which has in some instances terminated fatally.

The rare element THALLIUM ($Tl = 203.6$), which was discovered in 1861 by our distinguished countryman Mr. Crookes, F.R.S., is commonly classified with *lead*, chiefly owing to its close resemblance to the latter

in physical characters, high atomic weight, and the ease with which it can be precipitated by soluble sulphides and hydrochloric acid. Thallium is, however, a triad, and affords two chlorides, $TlCl$ and $TlCl_3$. The element colours the Bunsen flame a green colour, and the spectrum of the flame is distinguished by a beautiful green line of great intensity. It is met with in small quantity in many samples of copper pyrites and iron pyrites, but the only mineral in which it is yet known to occur in considerable quantity is an argentiiferous selenide of copper and thallium, termed *crookesite*.

CHAPTER XXXVI.

EXPERIMENTS WITH MANGANESE COMPOUNDS.

AMONGST the compounds of lead there are few so characteristic of the metal as the peroxide in its chemical relations, yet it is doubtful whether it has been met with in nature, though it is believed to form the mineral *plattnerite*. But a compound named *pyrolusite*, which very closely resembles lead peroxide in its composition and chemical characters, though not in appearance, is found native in large quantities. This is a peroxide of the metal manganese, consisting of MnO_2 , and is the *black oxide of manganese* we have already used in Experiments 57, 137, 138, 139, and others.

MANGANESE. $\text{Mn}^{\text{vi}} = 55$.

Experiment 499.—Pick out the purest obtainable pieces of pyrolusite and powder them, heat a portion in a test-tube with strong sulphuric acid, and note that a gas is evolved which is easily proved to be oxygen by the usual match test. The contents of the tube are heated for some time, and more of the peroxide is added should the first portion be completely acted upon, then allow the mixture to become cool, dilute with water and filter from undissolved peroxide. This *liquid*, if not impure from much iron¹ in solution,

¹ When the solution is brown coloured owing to the presence

can afford crystals of a pale rosy tint, consisting of $\text{MnSO}_4, 5\text{H}_2\text{O}$, or below 6°C. , $7\text{H}_2\text{O}$. Thus the action of sulphuric acid with manganese peroxide is analogous to that with lead peroxide, save that the manganese sulphate is soluble.



Experiment 500.—Repeat Experiment 137, and note that chlorine gas is evolved.¹ A corresponding change takes place with lead peroxide; but lead chloride is only slightly soluble, whereas manganese chloride is readily dissolved, and can be crystallised out from the solution; when purified from iron the crystals consist of the hydrated chloride $\text{MnCl}_2, 4\text{H}_2\text{O}$.

The product of the solution of crude black oxide of manganese in hydrochloric acid usually contains much iron, as well as free acid. The latter is removed from the filtered liquid by evaporation, and from the residue, when cold, the iron is separated as a reddish precipitate, by shaking up the liquid with some pure chalk, or calcium carbonate. The manganese chloride is not affected by the chalk, and remains in solution, while the soluble iron chloride is decomposed and its metal precipitated as a basic carbonate, which is removed by filtration along with the excess of chalk:

of iron, the latter can be removed as a hydrate by adding enough sodium hydrate to cause a permanent brownish precipitate, which is then filtered off. If the liquid which passes through the filter be still yellowish brown, a few drops more of the alkali must be added and the mixture again filtered. Care must be taken not to add too much sodium hydrate at first, else the manganese is precipitated as well as iron.

¹ See p. 156 for action on common salt.

used. This mode of separating iron from dissolved manganese is frequently employed in quantitative analysis, but it cannot be applied to a solution of the sulphate, or to the manganese salt of any acid radicle which can form a nearly insoluble salt with calcium.

The metal acts as a diad in the sulphate and chloride just prepared, but the other salts in which the element plays a similar part do not yet possess much practical interest, and need not be dealt with in this course ; it is only necessary to mention that they conform to the common type of such salts, and are not to be regarded as specially resembling those of lead.

Metallic manganese has been obtained in small quantity by reducing the oxide with charcoal in a black lead crucible, but the highest temperature of a powerful wind furnace is required for the operation, hence the experiment is one that can seldom be carried out. The product is a nearly white, brittle metal, of specific gravity 8 (water=1). It is so easily oxidised in air that it must be kept in vessels full of hydrogen or nitrogen. Manganese is not met with in commerce, but an alloy of it with iron and carbon termed *spiegeleisen* is largely used in steel manufacture, and is obtained on reduction by carbon of mixed oxides of iron and manganese.

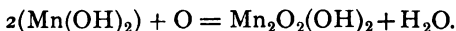
Experiment 501.—Add sodium carbonate solution to manganese sulphate or chloride. A white precipitate forms, which is carbonate of the metal $Mn^{++}CO_3$. The precipitate soon changes to a brownish colour if *exposed to the air*, as it absorbs oxygen and forms a *brown oxide*. When the unchanged carbonate is dried

and strongly heated in a current of hydrogen it leaves the oxide MnO as a greenish powder.

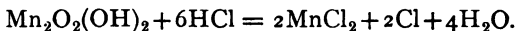
Experiment 502.—Instead of sodium carbonate add sodium hydrate to manganese sulphate solution; a white precipitate forms, which is not soluble in excess, and consists of the hydrate $\text{Mn}(\text{OH})_2$, corresponding to the oxide MnO ; this body rapidly changes to brown in air by absorption of oxygen.

When ammonium hydrate is used for precipitation instead of sodium hydrate, the precipitate first formed partially redissolves in excess, but it completely disappears if ammonium chloride be added to the liquid. The solution rapidly changes, however, by absorption of oxygen, and a brown precipitate of $\text{Mn}_2\text{O}_2(\text{OH})_2$ forms.

Experiment 503.—Precipitate some chloride of manganese by sodium hydrate, and shake up the hydrate $\text{Mn}(\text{OH})_2$ with air in a large jar. It is gradually converted into the brown body above noted, thus :—



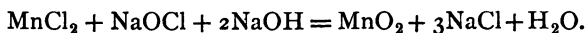
The hydrate so obtained by the atmospheric oxidation of the white precipitate is identical in composition with the mineral *manganite*, which is found in considerable quantities, and resembles pyrolusite in appearance. Like the latter it affords chlorine when *heated* with hydrochloric acid, and is therefore useful in the arts, though not so valuable as the peroxide



An anhydrous oxide, Mn_2O_3 , corresponding to *manganite*, is associated with manganese silicate in the

mineral *braunite*.¹ When the latter is *heated* with hydrochloric acid, chlorine gas is evolved. Lead sesquioxide acts in a similar way with hydrochloric acid, and the two oxides are probably analogous in constitution, but Mn_2O_3 , unlike the lead compound, unites with cold acids, and affords feeble salts of which Mn_2Cl_6 and $\text{Mn}^{\text{vi}}_2(\text{SO}_4)'_3$ are types.² In the instances noted of atmospheric oxidation of the hydrate $\text{Mn}(\text{OH})_2$ —or manganous hydrate—the peroxide is not obtained. It is obvious, however, that it should be possible to affect the synthesis of the peroxide by presenting a powerful oxidising agent to manganous hydrate at the moment of precipitation.

Experiment 504.—To solution of manganese chloride or sulphate add a strong solution of sodium hypochlorite and excess of sodium hydrate. A very dark brown precipitate forms, and this proves on analysis to be peroxide in a hydrated condition.³ The essential reaction is the following :—



The oxide thus precipitated, when rendered an-

¹ *Psilomelane* is the general name given to a group of somewhat indefinite manganese minerals which conform to the type of Mn_2O_3 , or of its hydrate manganite. The least hydrated contain barium in substitution for some of the manganese, while that most hydrated contains little barium, and is termed 'Wad' or 'bog manganese.'

² Here the hexad group Mn^{vi}_2 appears to result from the union of two tetrad atoms of manganese. These salts are termed *manganic*, and the former *manganous* compounds.

³ *Bromine water* also separates manganese as hydrated peroxide under these conditions

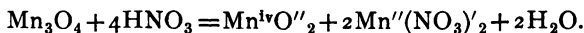
hydrous by heat, is identical in composition with the native pyrolusite. When very strongly heated it loses oxygen, as we shall find.

Experiment 505.—Place some of the powdered mineral peroxide in an iron tube closed at one end, heat the powder to redness. Gas issues from the tube, and is easily proved to be oxygen by the match test. When gas ceases to come off allow the tube to cool and turn out the contents, which are now brownish red instead of black. This product is another oxide of manganese, Mn_3O_4 , analogous in composition to red lead. It results from the following deoxidation by heat :—



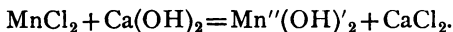
In the production of oxygen on the large scale the above process is sometimes adopted, but the high temperature required renders it objectionable for use in the experimental laboratory.¹

The oxide Mn_3O_4 occurs native as the mineral *hausmannite*. Like red lead, it affords chlorine when heated with hydrochloric acid, but in smaller proportion than any of the other oxides of manganese. This action suggests similarity to red lead in constitution as well as composition, and the result of treatment with diluted nitric acid confirms this view, as two-thirds of the manganese dissolves out as nitrate of the element in its diad condition, or manganous nitrate, and the rest is left as peroxide, *i.e.*, in the tetrad state:—

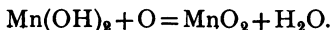


¹ The manganese peroxide used in the ordinary mode of preparing oxygen from potassium chlorate is not known to suffer any chemical change. See under Experiment 57.

A similar separation is effected by the acid in the case of the oxide Mn_2O_3 , or its hydrate, and it is inferred that the tetrad manganese present in each compound plays a feeble acidic part—in other words, that MnO_2 is the anhydride of an acid. Feebly saline compounds of the peroxide with powerful bases have actually been obtained, and it is probable that Weldon's successful process for the reconversion of the crude manganese chloride, obtained as a waste product in the manufacture of chlorine, into the valuable peroxide depends to some extent on the formation of such a compound with calcium. Weldon's process consists in treating the solution from the chlorine stills with excess of chalk, in order to precipitate iron, and then, after filtration or subsidence, with milk of lime, or calcium hydrate, when the following change occurs:—



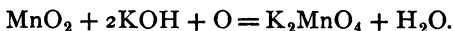
The hydrate of manganese separates mixed with unchanged calcium hydrate, and when suspended in the liquid is oxidised by a current of heated air, in which case



Without the excess of calcium hydrate the oxidation does not proceed so far, but in presence of the calcium hydrate a precipitate is obtained which contains calcium as well as manganese, and approaches CaMnO_3 in composition; this body is available for *use in the same way as the original peroxide in the preparation of a further quantity of chlorine.*

If, then, we regard manganese peroxide as the anhydride of a feeble acid, it is desirable to examine its action with a caustic alkali at high temperature.

Experiment 506.—Heat an iron spoon over a gas flame, and melt in it a small quantity of solid potassium hydrate or caustic potash. Then throw into the melted alkali a little finely powdered manganese dioxide, and stir with an iron wire. After heating for some time, the solid crust formed on the wire when cool is seen to have a *green* colour, and this is increased when enough manganese is added to make the mixture pasty. It is not desirable to heat the mass beyond low redness, but the production of the green body takes place more rapidly if a small crystal of nitre or of potassium chlorate be stirred in from time to time. When the product shows a deep green colour allow it to cool, and plunge the spoon and its contents into a small quantity of cold water. The green body dissolves readily to a green solution, while some unchanged peroxide is left. By very careful evaporation of the solution at low temperature it is possible to separate green crystals, which are found to contain K_2MnO_4 . Now the formula should be K_2MnO_3 if manganese peroxide and caustic potash only reacted, so that oxygen is taken up at the same time, either from the air or the oxidising agents (nitre or potassium chlorate) employed, and the essential reaction that occurs must be :—



The green body thus obtained is a true salt, termed

potassium manganate, but the dibasic acid corresponding to it, H_2MnO_4 —manganic acid—has not yet been isolated.¹

Experiment 507.—Dilute some of the green solution and boil it; note that the liquid changes from green to a magnificent *purple red* colour,² and the liquid on standing lets fall a brownish deposit which is easily proved to be manganese peroxide, while the solution becomes strongly alkaline, if it were not so before. The colour change noted has obtained for the green body the name ‘chameleon mineral,’ but the red colour is permanent on cooling. If the clear³ red liquid be evaporated to a small bulk, little dark red, or nearly black, crystals separate, and these when dried exhibit a fine greenish lustre resembling that of the wing-cases of some beetles. The empirical formula of the compound is KMnO_4 , and its name potassium permanganate.⁴ The body thus appears to differ from the manganate in but one particular, viz., in containing an atom less of potassium. We shall presently find, however, the theory requires the doubled

¹ The production of the green manganate serves as an excellent *test* for manganese. A little sodium carbonate is fused with the suspected body, and a crystal of nitre added when the green colour is developed.

² The addition of a little diluted sulphuric acid hastens the change.

³ The solution cannot be filtered through paper, as the latter decomposes the red compound. Asbestos is the best filtering medium if any need be employed.

⁴ This is the essential constituent of Condy’s disinfectant *liquid*, which is prepared on a large scale by a method identical *in principle* with that followed above,

formula $K_2Mn_2O_8$, and the decomposition of the manganate on boiling with water then is:—



The acid $H_2Mn_2O_4$ and its anhydride Mn_2O_7 have been obtained.

The chief reason for doubling the empirical formula of potassium permanganate is that, if written $KMnO_4$, we should be obliged to assume that in this particular compound manganese acts as an element of *uneven* atomicity, whereas in other compounds of the metal its atom acts with even atomicity, being either a diad, a tetrad, or perhaps hexad—the latter in the case of a hexafluoride, MnF'_6 , which is known to exist. When the formula of the permanganate is doubled the theoretic difficulty is removed, and the formation of the compound by the rearrangement of three molecules of the manganate is easily understood. The relative structure of the two compounds may be thus represented if we assume that in each the manganese atoms act with no higher than tetratomicity, and that both contain the diad¹ group $(MnO_2)''$, and the monad group $(K'O')'$.

Manganate.—



Permanganate.—



We already know, from the result of Experiment 302, that the permanganate easily parts with much of

¹ Diad, because two only of the four bonds or links of tetrad manganese are supposed to be engaged with the four of oxygen atoms acting as a diad chain, thus: $-O-O-$,

its loosely held oxygen; repeat the experiment in the following form :—

Experiment 508.—Add diluted sulphuric acid to solution of the permanganate, and note that no change of colour occurs ; now add to the mixture, drop by drop, diluted sulphurous acid, H_2SO_3 , and observe that the colour of the permanganate rapidly diminishes in intensity, and on continued addition of the sulphurous acid it wholly disappears, and a colourless liquid is obtained, which now contains only manganese sulphate, potassium hydrogen sulphate, and the excess of free sulphuric acid, partly resulting from the oxidation of sulphurous acid. Thus, in parting with its oxygen to sulphurous acid, the permanganate molecule is completely broken up, and the manganese rapidly reduced from the acidic, or electro-negative position, to the basic or electro-positive state, in which it acts as an apparent diad. This case is a type of similar oxidations effected by the permanganate, several of which are utilised with great advantage in quantitative chemical analysis. In neutral or alkaline liquids the reduction is not quite so rapid, nor does it proceed so far.

Experiment 509.—Agitate small pieces of filter paper with a solution of the crystals of permanganate, note that the paper is quickly stained brown,¹ and the colour of the solution steadily diminishes. Here the organic matter of the paper is readily acted upon by the permanganate and oxidised ; but the

¹ *The solution applied to the skin or fingers, or to linen, also causes brown stains*

reduction does not proceed beyond manganese peroxide, which constitutes the brown stain.

The action of the permanganate solution (Condy's fluid) as a *disinfectant* is due to the extraordinary ease with which it parts with more or less of its large store of oxygen to noxious materials, which are thereby burned up and destroyed. But it must be borne in mind that the permanganate is only effective when applied in solution, and in considerable quantity, to the infected matter. The solution also acts as a *deodorant*.

Experiment 510.—Add some permanganate solution acidulated with sulphuric acid to a small quantity of strong smelling sulphuretted hydrogen water. The colour is destroyed, and sulphur separates; if the permanganate be added until the colour no longer disappears quickly on shaking, the smell of sulphuretted hydrogen can no longer be perceived.

Permanganate solution diluted with much water is often used as a mouth-wash to remove foetor arising from decaying teeth.

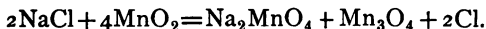
The above experiment may also be regarded from an analytical point of view, but is better conducted in a slightly different way by adding sulphuretted hydrogen water to permanganate solution acidulated with dilute hydrochloric acid; sulphur separates as before, and manganese chloride is left in solution, but no excess of sulphuretted hydrogen precipitates a sulphide of manganese from the acidulated liquid, nor does any manganese solution afford a precipitate of sulphide when the solution is acid.

Experiment 511.—Take a solution of pure man-

ganese chloride, add to it excess of ammonium hydrate, which redissolves the manganous hydrate precipitate (see Experiment 502), and then ammonium sulphhydrate. Note that a dull buff-coloured precipitate is thrown down. This is manganese sulphide, MnS . Throw the mixture on a filter, and wash with water; during the washing the precipitate darkens, owing to oxidation; remove a portion to a tube containing some diluted hydrochloric acid, and note that the precipitate dissolves almost completely, with evolution of sulphuretted hydrogen. The sulphide is soluble in the acid, and in almost all acids, and therefore cannot be precipitated from acid liquids, though, as we have seen, it is easily separated from *alkaline* solutions. It is the first metallic sulphide we have yet found to possess these characters. This sulphide is found native as *alabandite*.

Experiment 512.—Fuse some borax in a loop of platinum wire as in Experiment 321, add a minute fragment of pyrolusite and heat again, when a violet bead is obtained. Manganese peroxide is often used for colouring ordinary glass of an amethyst tint.

Note.—In the preparation of mercuric chloride (Experiment 453), some manganese dioxide was added to common salt in order that chlorine might be evolved; the change from which the chlorine results is thus represented:



This reaction can be used for the preparation of dry chlorine gas,

CHAPTER XXXVII.

EXPERIMENTS WITH CHROMIUM COMPOUNDS.

IN the course of our experiments a salt termed *potassium chromate*, K_2CrO_4 , has been frequently used as a test; this body is obviously similar in composition to potassium manganate, K_2MnO_4 . It contains the element CHROMIUM ($Cr = 54.2$), which resembles manganese to a certain extent in other particulars than in the production of the above-named salt, and may therefore be conveniently studied in this place.

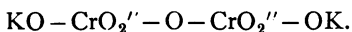
Potassium chromate is so easily purchased in a nearly pure condition that we shall use it in commencing our inquiry, and return later on to its manufacture, and to the preparation of the metal chromium.

Experiment 513. — Dissolve some potassium chromate in water (it is soluble in twice its weight of water), and boil the liquid. The solution does not change colour, and in this respect it is unlike the manganate (see Experiment 507). But we already know that the change from manganate to permanganate is facilitated by the addition of sulphuric acid, hence to the yellow solution of chromate add some *diluted sulphuric acid*, and note that the colour of

the solution at once changes to *orange-red*, and is not altered by further boiling—in fact, the colour change is due only to the action of the acid, and not to heat. Now evaporate the acidulated solution of the chromate to a small bulk, when crystals separate, but these no longer consist of the lemon-yellow chromate, and are fine orange-red prisms, which are found on analysis to consist of $K_2Cr_2O_7$ or ‘potassium bichromate,’ or dichromate. This body obviously results from the removal by sulphuric acid of half the potassium from two molecules of the chromate, thus :—



The orange-red salt is therefore derived from a new acid, $H_2Cr_2O_7$,¹ which contains an atom less of oxygen than permanganic acid ($H_2Mn_2O_8$), but which is probably similar in constitution to Nordhausen or anhydro-sulphuric acid $H_2S_2O_7$ (see Experiment 308). On this view the constitution of ‘potassium bichromate’ is :—



It is therefore more correctly termed potassium anhydro-chromate, and is sometimes written K_2CrO_4, CrO_3 . Large quantities of the salt are manufactured for use in dyeing and calico printing. It is obtained on the large scale by the method just employed, *i.e.*, by the

¹ Which has not been isolated. The salts of analogous *acids containing three* and even four atoms of chromium have been obtained.

action of sulphuric acid on the crude chromate (see under Experiment 528). Potassium bichromate is much less soluble in cold water than the neutral chromate; it requires ten times its weight at mean temperature, but it is dissolved by rather less than its own weight of boiling water. We shall presently find that the solution of the neutral and bichromate can act as powerful oxidising agents.¹

Experiment 514.—Add silver nitrate to solution of either neutral or bichromate, and note the production of a brick-red silver chromate in each case, as in Experiment 444. This precipitate is easily dissolved by dilute nitric acid.

Experiment 515.—Make a similar experiment with lead nitrate or acetate, and note the production of *chrome yellow*, as in Experiment 491. If the precipitate be boiled with sodium hydrate a reddish basic chromate is obtained, which is used as a pigment, and termed *chrome red*.

Experiment 516.—Test another portion with barium nitrate solution, and note that a yellow pre-

¹ The bichromate is easily reduced by light in presence of organic matter; if the latter be gelatine, a body insoluble in warm water is formed. The process of photographic *carbon printing* depends on this fact. A gelatine layer coloured with indian ink (carbon finely divided), and sensitised with bichromate, is formed on paper or other suitable material. When dry it is exposed to light under a *negative*, and when sufficiently acted upon the film is treated with warm water, which dissolves away the unacted upon gelatine layer, and leaves clean the white paper, which then forms the lights of the picture, the shadows being formed by the insoluble gelatine and pigment.

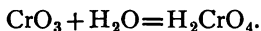
cipitate of BaCrO_4 is produced, which is easily soluble in dilute nitric or hydrochloric acid.

Silver, lead, and barium nitrates are thus convenient tests for soluble chromates. Many other chromates are known, but are not yet of much importance. Experiment 513 has already shown that dilute sulphuric acid removes part of the potassium from the neutral chromate; we shall now examine the effect of a large excess of the acid upon the bichromate.

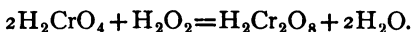
Experiment 517.—Take a *cold* saturated solution of potassium bichromate, prepared as in Experiment 73, place it in a porcelain dish, and add gradually to it strong oil of vitriol, stirring well with a glass rod. For every 10 c.c.s. of bichromate solution used, 14 c.c.s. of strong acid should be added. Allow the mixture to cool, and fine orange-red crystals will separate; after some hours drain off the acid liquid, and transfer the crystals by means of a glass rod to a funnel, in whose throat is a light plug of asbestos;¹ cover the funnel with a glass plate. The removal of the last traces of sulphuric acid is a very troublesome operation, but can be effected by washing with strong nitric acid and drying in a current of air. The red crystals are found on analysis to consist of CrO_3 . This body is very deliquescent even when free from all traces of sulphuric acid. It forms with water an acid liquid from which the chromates are easily derived; it is to be inferred, therefore, that chromium trioxide is the anhydride of chromic acid, though the latter has not been actually isolated.

¹ *Used because of the corrosive action of the crystals as well as of the sulphuric acid on paper, wool, &c.*

Experiment 518.—Dissolve a crystal or two of the anhydride in water, and produce chromic acid :—



Now add a few drops of hydrogen peroxide solution, and note the fine blue colour developed. If a few drops of ether are shaken up with the mixture the blue compound dissolves in the ether, and the latter rises to the surface of the mixture strongly coloured. This is in effect a repetition of Experiment 78. The blue solution is supposed to contain perchromic acid—the analogue of permanganic acid, $\text{H}_2\text{Mn}_2\text{O}_8$ —thus formed :—

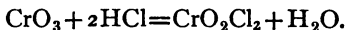


Perchromic acid is a very unstable body, and has not been isolated.

Experiment 519.—Add some crystals of the anhydride to a small quantity of sulphuric acid contained in a test-tube ; dissolve as much as possible by occasional agitation, but without applying heat. Now hold the test-tube under a flue and add some strong hydrochloric acid drop by drop. On the addition of the first drop the liquid assumes a red colour, much heat is evolved, and very irritating vapours arise which *must not be inhaled* ; successive additions of hydrochloric acid increase the colour, and blood-red droplets of a liquid are seen to condense on the sides of the tube. This volatile fuming liquid, when prepared on a larger scale, and analysed in a pure state,¹

¹ The liquid is conveniently prepared in quantity by distilling a thoroughly dried mixture of equal weights of common

is found to have the composition CrO_2Cl_2 , and is termed chlorochromic anhydride, *i.e.* chromic anhydride whose oxygen is partly replaced by chlorine. It results from the action of hydrochloric acid on the anhydride thus :—



When aqueous hydrochloric acid is used alone this body is not formed (see Experiment 529). The sulphuric acid above employed attracts the water of the aqueous hydrochloric acid, and prevents interference with the reaction. When liquid chlorochromic anhydride is mixed with water it is decomposed, chromic and hydrochloric acids resulting. The acid corresponding to this anhydride is not yet known, but a potassium salt, KOCrO_2Cl , is produced by saturating warm hydrochloric acid with potassium bichromate ; the salt crystallises on cooling. Chlorochromic anhydride may be viewed as chromyl dichloride, *i.e.*, as the dichloride of the diad group CrO''_2 , or 'chromyl.' The constitution of this compound, and of all the compounds of chromium hitherto dealt with, could be explained without assuming the metal to be other than a tetrad element, but the existence of a hexafluoride, CrF_6 , is evidence that chromium, like manganese, can act with the higher atomicity, and it may so act in chromic and chlorochromic anhydrides, chromic and perchromic acids and their salts.

salt and potassium bichromate with excess of sulphuric acid. *The production of chlorochromic anhydride in this way renders the process a test for either a chloride or a chromate.*

Experiment 520.—Heat a few crystals of the anhydride in a porcelain crucible. Note that the body melts to a deep red liquid, and on further heating (to 260° C.) oxygen gas is evolved, and a green powder is left. The latter consists of Cr_2O_3 . Thus chromium trioxide easily parts with half its oxygen :—

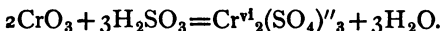


This explains its powerful oxidising action already noticed, especially on organic substances such as paper, wool, animal tissues, alcohol, &c.

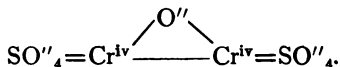
Experiment 521.—Pour a few drops of strong spirit of wine into a porcelain dish, and spread the liquid over the surface, then throw in a few crystals of the anhydride ; if the spirit be strong and not present in too large quantity, the violence of the oxidising action that ensues will cause the alcohol to burst into flame. Combustion is more easily induced by allowing a few drops of alcohol to fall from a spoon on some crystals of the anhydride. We shall now employ the anhydride for the oxidation of a body in solution, the compound oxidised being sulphurous acid.

Experiment 522.—Take some freshly prepared sulphurous acid solution, which should be free from sulphuric acid, as proved when a portion is tested by the method followed in Experiment 298. Now throw in some crystals of pure chromic anhydride. Note that a beautiful *green* liquid is at once produced, and if the addition of the anhydride be continued a point is reached at which the odour of sulphurous acid disappears, and the liquid can be shown by the barium

nitrate test to contain sulphuric acid. If the solution be acid and allowed to stand in the cold for a long time (some weeks), it slowly changes to a violet colour; the solution is found to contain the compound $\text{Cr}_2(\text{SO}_4)''_3$, or chromium sulphate, which results from the following elegant reaction:—

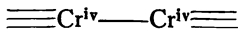


When the violet solution is boiled it again becomes green, and the liquid, when evaporated to dryness, affords an uncrystalline green residue, which dissolves very slowly in water, and consists of $\text{O}''\text{Cr}^{\text{I}}_2(\text{SO}_4)''_2$. Or:—



Thus the violet sulphate is the normal salt, and the green body is a basic compound.

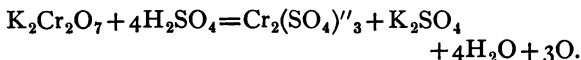
In the action of sulphurous acid or chromic anhydride we have evidence of the reduction of chromium from acidic or electro-negative to the electro-positive condition, and coincident with this an apparent change in atomicity. But the reduction does not proceed as far as with manganese,¹ since each chromium atom is *still tetrad* in both sulphates, one atom united with another of the element, and forming the *hexad group* of two atoms, thus:—



¹ A group of chromium salts analogous to MnCl_2 , MnSO_4 , &c., is known, but they are not found in reactions similar to those above given (see p. 170).

A similar reduction is effected when either chromic anhydride or potassium bichromate is heated with strong sulphuric acid ; in each case oxygen gas is evolved.

Experiment 523.—Powder some potassium bichromate, introduce it into a flask, and add enough strong sulphuric acid to make the powder into a very thin paste, then warm carefully. Gas is soon evolved, which is easily collected and identified as oxygen if a cork and delivery tube be fitted in the usual way to the flask. When gas ceases to pass off remove the cork from the flask, allow the contents to cool, and then throw into water ; a green solution is obtained which contains chromium sulphate, resulting from the following change :—

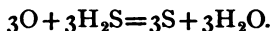


When the solution is allowed to evaporate slowly octahedral crystals separate. These are found to consist of the two sulphates in chemical union, along with water, forming the compound termed ‘chrome alum,’ $\text{K}_2\text{SO}_4, \text{Cr}_2(\text{SO}_4)_3, 24\text{H}_2\text{O}$.¹ The crystals are deep violet in colour, and form a solution of a somewhat similar tint, which becomes green on boiling.

Experiment 524.—To a solution of the bichromate add a few drops of diluted sulphuric acid and heat, but no change occurs, as the reduction does

¹ For the general characters of this group of bodies termed ‘alums’ see ALUMINUM.

not take place unaided in *dilute* solution. Now pass a current of sulphuretted hydrogen gas through the liquid,¹ or add H_2S water, and note that the solution becomes green, while a white precipitate is formed—the latter is only sulphur. In this case the three atoms of oxygen, which we know from the last experiment to be available, are used in decomposing three molecules of sulphuretted hydrogen, thus :—



Sulphuretted hydrogen does not precipitate chromium from acid or alkaline solutions when the metal is in the basic condition, and a sesquisulphide of the element has not been formed in the wet way, though it can be produced on heating chromium with sulphur. If, however, sulphuretted hydrogen be passed through a solution of potassium bichromate, to which excess of ammonium hydrate has been added, a brown precipitate is produced, which is believed to consist of Cr_2S_7 —the sulphur representative of the unknown perchromic anhydride—but the body decomposes very easily, and its composition is somewhat doubtful.

Experiment 525.—To a solution of chromium sulphate, obtained as in Experiment 522 or 523, add sodium hydrate. A bluish-green precipitate is produced, which essentially consists of chromium hydrate, $\text{Cr}^{\text{VI}}_2(\text{OH})'_6$. This body dissolves in excess of

¹ Sulphurous acid, alcohol, and many other bodies, especially iron salts (see IRON), act in a similar way as reducing agents.

alkali, and forms a fine green solution. Now heat the latter slowly to boiling, and after continual boiling—which must be very carefully conducted, as the liquid ‘bumps’ violently—the whole of the chromium is again precipitated as a lower hydrate, and a colourless liquid is left.

Experiment 526.—Add ammonium hydrate to chromium sulphate solution, a greenish or pale violet precipitate of the hydrate forms; but this is very slightly soluble in excess in the cold and not at all on heating. When the hydrate is dried and heated to 200°C . in hydrogen gas the compound $\text{Cr}_2\text{O}_2(\text{OH})_2$ remains. This body may obviously be written $\text{H}_2\text{Cr}_2\text{O}_4$. Alkaline carbonates precipitate a carbonate analogous in constitution to the basic sulphate; the precipitate is soluble in large excess.

Experiment 527.—Collect on a filter some of the hydrate precipitated by ammonium hydrate, wash with water, and dry. Then ignite the dried hydrate in a porcelain crucible; water is evolved and a dull green body left, which consists of chromium sesquioxide, Cr_2O_3 . This body is used as a pigment named ‘chrome green.’¹ When required for this purpose, however, it can be obtained of a brighter tint by igniting mercurous chromate, which is easily decomposed by heat, affording mercury, oxygen, and a residue of chromium sesquioxide. The anhydrous

¹ Another ‘chrome green’ of a fine rich tint is obtained by strongly heating a mixture of one part bichromate and three of powdered gypsum, $\text{CaSO}_4, 2\text{H}_2\text{O}$; when the product is boiled with diluted hydrochloric acid a very stable green powder is left, and is not affected by acids or light.

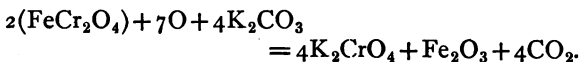
oxide is very slightly soluble in acids, especially after ignition, and when in this condition it is best rendered soluble by fusion with potassium acid sulphate, KHSO_4 .

The facts observed in the course of these experiments lead to the conclusion that while chromium sesquioxide—or chromic oxide as it is shortly called—is a basic anhydride, its hydrate is capable of acting as a very feeble *acid*, especially in presence of strong bases, *e.g.*, sodium, potassium, iron, &c. ; the sodium and potassium salts are formed as in Experiment 525, but the iron salt is met with in nature as the most important of the mineral compounds of chromium, termed *chrome iron ore*, FeCr_2O_4 . This may be regarded as the iron salt of the hydrate $\text{H}_2\text{Cr}_2\text{O}_4$ already referred to under Experiment 526, as resulting from the partial dehydration of $\text{Cr}_2(\text{OH})_6$. It is, then, this latter hydrate that acts as an acid—*chromous acid*.

The iron chromite is easily converted into iron chromate by oxidation, and the latter decomposed so as to afford potassium chromate and iron oxide. The oxidising agent usually employed is nitre.

Experiment 528.—Reduce to fine powder some chrome iron ore, which can be easily purchased, mix it with an equal weight of nitre, and a similar quantity of potassium carbonate, and pour the mixture into a small fireclay crucible. Heat the latter as strongly as possible in a good fire for ten minutes, *when cold break the crucible and pick out the fused material, which is then to be boiled with water ; note*

that a yellow solution is obtained, from which potassium chromate can be crystallised and identified as already pointed out, while a dark reddish brown residue, consisting of a sesquioxide of iron, Fe_2O_3 , remains undissolved together with any grains of the chrome ore which may have resisted chemical change, as it is a body which is difficult of decomposition. In this reaction ¹

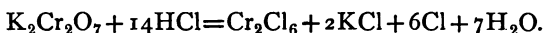


On the large scale nitre is not used, as the mixture of chrome ore and potassium carbonate, with the addition of some lime, is roasted in an air current whose oxygen then acts as that of the nitre in our experiment; the lime used facilitates the action partly by removal of CO_2 from the potassium carbonate, and partly by preventing fusion of the mass and thus rendering oxidation more rapid. The product is extracted by water, from which potassium chromate is crystallised out. The normal chromate is converted into bichromate by the means employed in Experiment 513.

Experiment 529.—Add a few crystals of chromic anhydride to some strong hydrochloric acid in a test-tube and warm; note that chlorine gas is evolved, and the liquid changes in colour from reddish yellow to

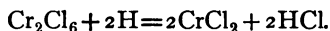
¹ Any body suspected to contain chromium may be tested for the element by fusion in a piece of platinum foil with nitre and potassium or sodium carbonate. The whole is boiled with water in a test-tube, the liquid filtered, and if yellow tested with lead or silver nitrates, after neutralising the alkali by acetic acid.

bright *green*, and a portion of the solution when tested with ammonium hydrate gives the usual pale bluish-green precipitate of chromic hydrate. When the solution is evaporated to a small bulk green needle-like crystals can be obtained, which contain $\text{Cr}^{\text{VI}}_2\text{Cl}_6$, $12\text{H}_2\text{O}$. The same body is produced by dissolving chromic hydrate in hydrochloric acid, and along with chlorine gas by the action of strong and boiling hydrochloric acid on the bichromate



The hydrated chromic chloride when gradually heated in a porcelain tube in a current of chlorine gas loses the water and leaves a pale violet residue, which sublimes at a very high temperature, and can be then obtained in crystalline scales consisting of Cr_2Cl_6 , which dissolve very slowly even in boiling water, but ultimately afford a green solution.

When chromic chloride is heated in a current of pure hydrogen gas the molecule loses two atoms of chlorine, and the compound CrCl_2 is left, thus :—



This body is termed *chromous chloride*, and is white ; it dissolves in water forming a blue coloured liquid, which absorbs oxygen quickly, and reforms a chromic salt. Chromous chloride affords the hydrate $\text{Cr}(\text{OH})_2$, an oxide, CrO , and is a type of another class of chromium compounds in which the metal acts as an apparent diad, like manganese in its chloride MnCl_2 , *but the study of this group of chromium salts may best be reserved for the advanced course.*

Molybdenum, Tungsten and Uranium. 171

We have thus met with three oxides, CrO , Cr_2O_3 , and CrO_3 ,¹ with the chlorides CrCl_2 and Cr_2Cl_6 , and the fluoride CrF_6 —types of compounds in which chromium acts as a diad, tetrad, and hexad element. The METAL itself is rarely seen, and is obtained only with great difficulty by heating, in a powerful wind furnace, an intimate mixture of sugar, charcoal, and chromium sesquioxide. It is a white metal of sp. gr. 6·8, extremely hard, and difficult of fusion, being little less fusible than platinum. It is not attacked by nitric acid, but is soluble in diluted sulphuric acid, with the formation of chromous sulphate, hydrogen being displaced. This metal is not of any practical importance as yet.

The rare metals related to chromium are:—
MOLYBDENUM, $\text{Mo} = 95\cdot5$, whose mineral sulphide— MoS_2 , *molybdenite*—is the chief source of the element;
TUNGSTEN (*Wolframium*), $\text{W} = 183\cdot5$, is chiefly met with in the mineral *wolfram* (FeMn), WO_4 ; and
URANIUM, $\text{Ur} = 240$, whose principal compound is *pitchblende*, an impure oxide.

¹ Other less important oxides are known, viz., a brown body, Cr_2O_3 , CrO_2 , which may be regarded as chromic chromate, and $\text{Cr}''\text{Cr}_2\text{O}_4$, or chromous chromite, analogous to chromic iron.

CHAPTER XXXVIII.

EXPERIMENTS WITH IRON AND ITS COMPOUNDS.

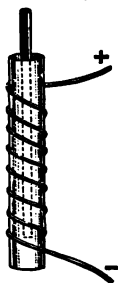
IRON, Fe^{IV} (*ferrum*) = 56.—Metallic iron occurs in very small quantity in the earth's crust, and then either as scattered grains throughout some of the basaltic rocks, or partially alloyed with the metal *nickel*, in the meteoric masses occasionally met with on the earth's surface. On the other hand, compounds of the metal are found almost everywhere, but the number of those from which the metal is extracted for use in the arts is very small. Of these the most important are *red hæmatite*, *brown hæmatite*, *clay ironstone*, and *magnetic oxide of iron*. From one or other of these ores is the metal extracted by methods which will be described at the end of this chapter. For the present we shall take as an example of nearly pure iron the best soft wire obtainable, as it is extremely difficult to prepare on the small scale a specimen of the metal which can compare in purity with either the finest commercial iron wire or that which has been hardened for use as pianoforte strings.

Iron is greyish-white in colour, malleable when pure, and easily drawn into fine wire, which is of *great strength*. The specific gravity of the metal is 7.8 (*water* = 1). It is attracted by a magnet, espe-

cially when cold, but even when long in contact with a magnet it does not permanently acquire magnetic properties if it be pure. It is temporarily magnetised under the influence of the galvanic current.

Experiment 530.—Coil some copper wire round a rather wide glass tube and pass a rod of *wrought* iron into the tube, so that one end may project, as in fig. 127. Bring near to the rod some tacks or small nails, and note that the iron does not attract them. Now connect the ends of the copper wire with those of a galvanic cell or battery. The iron core now attracts the tacks and retains them until the rod is withdrawn from the tube and thus removed from the influence of the current, or the battery connection is broken and the electric current no longer circulates.

FIG. 127.

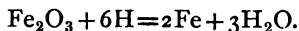


Experiment 531.—Heat one end of a piece of iron wire in the flame of the blowpipe, and note that the metal softens and partially fuses at a white heat. Pure iron requires a full white heat for fusion, and we already know from Experiment 65 that it can be easily melted in the oxyhydrogen flame, wherein it also burns with great brilliancy. If two thin wires are crossed, strongly heated in a reducing flame at the point of contact, and then squeezed together, partial adhesion of the pieces of metal takes place. This union under pressure only occurs when the metal is in a pasty condition and clean surfaces are presented to each other. Effective union of this kind under pres-

sure is termed 'welding,' and is a property of the metal which greatly facilitates working it in considerable masses.

When strongly heated with free exposure to air, as a blacksmith works the metal, or when iron wire is heated in oxygen, as in Experiment 61, a black scum forms on the surface of the iron, and can be broken off in scales. This is an oxide of the metal, consisting of Fe_3O_4 . This body is identical in composition with the oxide resulting from the action of steam on iron at a high temperature, as in Experiment 48, and is not subject to further change. At low temperatures iron articles do not oxidise in pure dry air, but oxidation, or 'rusting,' proceeds with moderate rapidity if the air be moist and contains carbon dioxide gas, or traces of any acid.¹

Experiment 532.—Collect some iron rust and heat it in a small porcelain crucible to drive off water; then powder the residue, which now consists of the red oxide Fe_2O_3 . Heat this powder strongly in an atmosphere of hydrogen, as in Experiment 53, and metallic iron in a fine state of division results:—



The black or greyish-black powder obtained is the *Ferrum reductum*, B.P., or *fer réduit*, which is pyrophoric, for if poured out into the air when warm the powder becomes incandescent, owing to rapid union of

¹ This can be prevented by Barff's patent method, which consists in coating the metal with a layer of the oxide Fe_3O_4 , by heating to redness in an atmosphere of steam.

the metal with the oxygen of the air. After a time the finely divided metal ceases to take fire spontaneously in air, owing doubtless to slight superficial oxidation of the particles, but it must at all times be preserved in well-stoppered bottles. The powder is easily attracted by a magnet.

Reduced iron may be confounded with the black oxide of the metal Fe_3O_4 , but it is quickly distinguished by the addition of a small quantity of diluted hydrochloric acid, when hydrogen gas will be evolved with effervescence¹ if the body contains metallic iron, but no effervescence occurs with the oxide. Again, when shaken up with water coloured of a yellow tint by free iodine the solution is decolourised.²

The most convenient source of iron compounds is the metal as met with either in the best wrought-iron wire or in carpenter's tacks. Either form may be used in any of the following experiments in which the metal is employed.

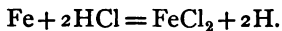
Experiment 533.—Dilute hydrochloric acid in a beaker with an equal volume of water, and add iron to the liquid. The metal dissolves rapidly and gas is evolved, which is easily proved to be hydrogen.³ Add more iron until all evolution of gas ceases, then filter quickly into a bottle provided with a good stopper, and preserve the solution. The liquid has a bluish-green colour, and even when largely diluted with

¹ See Experiment 533.

² See Experiment 536.

³ Hydrogen thus generated has usually an unpleasant smell. This is in great part due to the formation of strong-smelling hydrocarbides, produced by the union of nascent hydrogen with the carbon found in the purest specimens of wrought iron.

water, it has a taste which is commonly described as 'inky.' When this solution is evaporated over oil of vitriol in the exhausted receiver of an air-pump, it can be made to afford greenish crystals, which consist of $\text{FeCl}_2, 4\text{H}_2\text{O}$. The action of iron on hydrochloric acid may therefore be thus explained :—

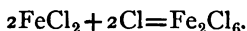


The iron chloride thus formed unites with four molecules of water in crystallising.

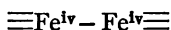
Iron thus acts as a diad in this chloride, and in so far resembles manganese, chromium, &c., in the manganous and chromous chlorides. Unlike the former, however, the iron chloride solution quickly changes to a yellowish-brown colour by the action of the air, other oxidising agents, or of chlorine in acid liquids ; but in this respect it rather resembles chromous chloride, which is also very prone to change. If the analogy with the latter rather than with manganous chloride be true, the iron salt obtained in the course of our experiment should afford a higher chloride analogous to Cr_2Cl_6 on treatment with chlorine.

Experiment 534.—Conduct a current of chlorine gas, produced as in Experiment 139, into a portion of the solution of iron chloride, already prepared. Note that the colour quickly changes, even without heat, to a yellowish brown, or a yellow tint, if the liquid contains but little iron. When the solution smells strongly of chlorine, even after shaking, stop the current of gas and gently heat, in order to expel all unnecessary

chlorine. When some of this solution is now evaporated to a small bulk and allowed to cool over oil of vitriol, a reddish yellow crystalline mass is obtained, which is a hydrate of the iron chloride, whose empirical formula is FeCl_3 , but which we write Fe_2Cl_6 , for reasons to be presently stated. Hence the action of chlorine on the iron solution may be thus represented:—



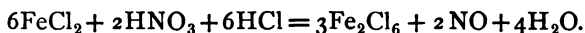
The new chloride is similar in composition to chromic chloride, Cr_2Cl_6 . The nomenclature of the compounds is also analogous to that of the chromium chlorides; thus FeCl_2 is *ferrous* chloride, and Fe_2Cl_6 *ferric* chloride. Moreover, the constitution of the latter body must be explained in the same way as that of chromic chloride, for iron is diad in ferrous compounds, though an apparent triad in ferric chloride, and, since it is contrary to experience that an atom of an element can act with both even and uneven atomicity, we conclude that it is really a *tetrad* or four-link element, and that it acts as such in the ferric compounds, two tetrad iron atoms uniting to form the *hexad group*, Fe_2^{VI} , thus—



The anhydrous ferrous chloride is obtained as greenish white, or nearly colourless, crystals by heating metallic iron very strongly in hydrochloric acid gas; it is converted into vapour at a high temperature, and may be sublimed, but with difficulty. Anhydrous *ferric chloride* is obtained by heating iron in an excess

of chlorine gas ; combination occurs, much heat is evolved, and a sublimate, consisting of greenish-black and very deliquescent crystals, is obtained. The specific gravity of the vapour of this body is 1.65 ($H=1$), therefore its molecular weight is 330, which is sufficiently close to the theoretic number 325 for Fe_2Cl_6 to leave no doubt as to the correctness of the formula.

Ferric chloride is dissolved by alcohol ; and an alcoholic solution is commonly used in medicine under the name of *muriate tincture of iron*, or *tinctura ferri perchloridi*, B.P. The process directed by the 'Pharmacopœia' is identical in principle with that followed above, the first step being the production of a strong solution of ferrous chloride by dissolving iron wire in hydrochloric acid. This solution, which must contain an excess of acid, is then treated with nitric acid, and the mixture briskly heated in a capacious evaporating dish until, on the sudden evolution of red fumes, the liquid changes from a nearly black colour to orange brown ; the solution is then evaporated in order to drive off excess of acids, and the product diluted with water to form the *liquor ferri perchloridi fortior*, B.P., or with rectified spirit of wine to form the *tincture*. The former contains one part, by weight, of iron, in five parts by volume ; the tincture one part of iron in twenty of a mixture of five parts water and fifteen of spirit. The following equation represents the change effected by nitric acid in solution of ferrous chloride :—

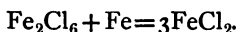


When nitric acid is added to the ferrous chloride

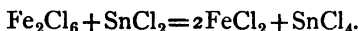
solution, NO is the immediate product of reduction by the ferrous salt, the excess of which latter dissolves the nitric oxide and forms therewith a compound analogous to that directly produced in Experiment 107c; but NO gas is not soluble in *ferric* chloride; hence when the conversion of ferrous into ferric chloride is complete the previously dissolved gas is suddenly evolved with much frothing, so that a relatively large and wide vessel should be used in the preparation.¹

Ferric oxychlorides are known, e.g. $\text{Fe}^{\text{I}}_2\text{O}''\text{Cl}_4$ and $\text{Fe}^{\text{I}}_2\text{O}''_2\text{Cl}'_2$.

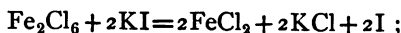
Experiment 535.—Introduce into a well-stoppered bottle some iron wire; then pour over the wire aqueous solution of ferric chloride, freed from excess of acid by evaporation, stopper the bottle, and leave it aside. The yellowish or brownish colour of the ferric salt soon leaves the solution, and it becomes pale green, indicating *reduction* to ferrous chloride, a conclusion that can be confirmed by the distinctive tests given at p. 186. The change is of the following kind :—



Ferric chloride is also reduced by stannous chloride, thus :—

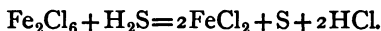


By potassium iodide, thus :—



¹ It is interesting to note that ferric chloride solution is of a deeper colour when hot than when cold.

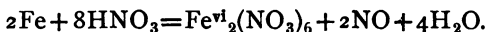
and by many other bodies—*e.g.* sulphurous acid, sodium thiosulphate, and sulphuretted hydrogen ; in the latter case



Experiment 536.—Place in a large test-tube about one gramme of iron and add two grammes of iodine in powder, followed by 5 c.cs of water ; then warm gently, and note that the colour of the iodine gradually disappears ; on finally boiling the combination is complete, and some iron remains undissolved. The liquid when filtered is of a pale greenish colour, and contains the compound FeI_2 , a ferrous iodide, thus obtained by direct union of the elements even in presence of water. This solution, when mixed with a strong syrup of white sugar, forms the *syrupus ferri iodidi*, B.P. Ferrous iodide when in simple aqueous solution is easily decomposed by atmospheric oxygen ; but the presence of sugar is found to diminish the tendency to change. A spiral iron wire placed in the liquid serves, as in the last experiment, to reduce any ferric salt that may happen to be formed by atmospheric oxidation. The anhydrous ferrous iodide can be obtained as a fused product by heating iron with excess of iodine in a crucible ; a ferric iodide is probably formed in the first instance, but decomposed by heat into free iodine and ferrous iodide. Bromides and fluorides of iron are also known.

Experiment 537.—Add iron wire in small portions to a mixture of one part of strong nitric acid and five of water ; action soon commences and the metal dissolves, while much nitric oxide gas is evolved.

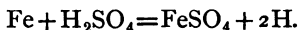
The solution is of a clear reddish-brown colour, and constitutes the *liquor ferri pernitratis*, B.P. The compound $\text{Fe}_2(\text{NO}_3)_6$ can be separated from the liquid ; it is formed thus :—



When solution of ferrous chloride is precipitated by silver nitrate, a liquid is obtained on filtration, which for a short time contains a greenish ferrous nitrate.

Iron plunged into strong nitric acid is not dissolved, and assumes a curiously indifferent or *passive* condition.

Experiment 538.—Dissolve iron to saturation in diluted sulphuric acid ; hydrogen gas is freely evolved, and the solution of the metal when filtered is of a pale bluish-green colour ; this liquid when slowly evaporated affords fine crystals of hydrated ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. When the metal dissolves in the diluted acid,

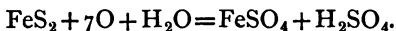


The commercial salt is termed ‘copperas’ or ‘green vitriol,’ and is used in ink making,¹ dyeing,² and for many other purposes ; it is obtained on the large scale by the atmospheric oxidation of the sulphide of

¹ Ordinary black writing ink is prepared by adding solution of ferrous sulphate to infusion of nut-galls. A black gallo-tannate of iron is formed in solution, and the liquid, when slightly thickened by the addition of gum-arabic and some sugar, can be used in writing. *Tincture of nut-galls* is a convenient test for iron, as it produces a black colour as above.

² The common black dye for coarse materials is obtained by adding ferrous sulphate to logwood infusion.

iron or pyrites met with in the coal measures. The following decomposition occurs:—



The products dissolve in water and the solution is allowed to act on scrap iron, when the sulphuric acid is converted into a further quantity of ferrous sulphate, and the whole liquid is evaporated and crystallised. Hydrated ferrous sulphate crystals are, when pure, of a beautiful bluish-green colour. They are easily soluble in water, but insoluble in alcohol. A stable compound of ferrous and ammonium sulphates, which is much less subject to oxidation than ordinary ferrous sulphate, is easily prepared and much used in quantitative analysis.

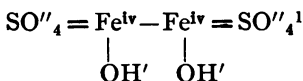
Experiment 539.—Dissolve crystals of ferrous sulphate mixed with half their weight of ammonium sulphate in sufficient boiling water to get the mixture into solution, then filter the liquid and let it cool. Fine pale bluish-green crystals will separate on cooling, and these when drained, pressed between folding blotting-paper, and quickly air-dried, are found to consist of $\text{FeSO}_4, (\text{NH}_4)_2\text{SO}_4, 6\text{H}_2\text{O}$. It is worthy of note that this salt when pure and dry contains exactly *one-seventh* of its weight of iron in the ferrous condition.

Experiment 540.—Take a hot saturated solution of ferrous sulphate (boiling water dissolves rather more than three times its weight of the salt), and pour it slowly and with constant stirring into its own *volume of rectified spirit* (recently distilled methylated

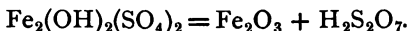
spirit may be used), when a granular crystalline deposit forms. This is the *ferri sulphas granulata*, B.P., and is identical in composition with the ordinary salt, differing only in size of crystals.

Experiment 541.—Powder some ordinary ferrous sulphate and place it in a porcelain capsule, and the latter in an oven which can be heated to a temperature of 150°C . Water is evolved, and the heat must be continued until evolution of water vapour ceases; the residuum is yellowish white, and approaches in composition to the formula $\text{FeSO}_4, \text{H}_2\text{O}$. This product is the *ferri sulphas exsiccata*, B.P. The last molecule of water of crystallisation is removed with difficulty, and, under ordinary pressure, its removal by heat is accompanied by more or less decomposition of the iron sulphate.

When this dried salt is heated for some time in contact with air it absorbs sufficient oxygen to become



And this body when strongly heated in clay retorts affords Nordhausen or fuming oil of vitriol (see under Experiment 308) and ferric oxide, thus:—

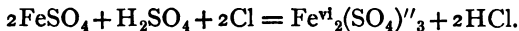


Ferrous sulphate solution readily undergoes change on exposure to the air, similar to that observed in the

¹ This is but one of several basic ferric sulphates known to exist.

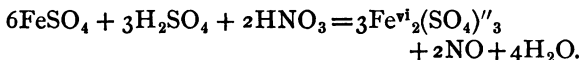
case of the chloride, and gradually becomes brownish, owing to conversion into a ferric salt. When free sulphuric acid is present chlorine easily and completely converts a solution of ferrous into one of ferric sulphate.

Experiment 542.—Dissolve ferrous sulphate in water, strongly acidulate the solution with sulphuric acid, and pass a current of chlorine through the liquid: a brownish red colour is developed; when the solution smells strongly of chlorine boil to expel the excess of the gas. This solution now contains the ferric sulphate corresponding to the chloride produced in Experiment 534, together with hydrochloric acid. The action of the chlorine is thus explained:—



When the solution is evaporated the hydrochloric acid is expelled, and a syrupy liquid obtained which slowly deposits crystals of the sulphate.

The *liquor ferri persulphatis*, B.P., is prepared by an analogous process, nitric acid instead of chlorine being used (as in the case of ferric chloride) to effect the conversion of the acid solution of ferrous sulphate into the ferric salt; the reaction is:—

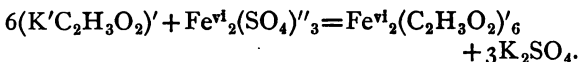


Thus in *ferrous* chloride and sulphate, and *ferric* chloride and sulphate we have types of two great *classes of iron* compounds; the first, or ferrous salts, are usually green or bluish green, whereas the ferric

compounds, or 'persalts' as they are often termed, are usually brown or reddish brown.

From the solution of ferric sulphate the *tinctura ferri acetatis*, B.P., is thus easily obtained by double decomposition.

Experiment 543.—Dissolve some potassium acetate in rectified spirit of wine, and add an equal volume of solution of ferric sulphate, shake and allow the mixture to stand for an hour. A precipitate is formed which consists of potassium sulphate, a salt which is very slightly soluble even in diluted spirit, while ferric acetate remains in solution. In this case



If the molecular proportions are used the spirit will contain only ferric acetate. The solution decomposes after some time or more rapidly on heating, acetic acid being separated while a basic ferric acetate precipitates.

'Acetate of iron liquor' is used by dyers as a mordant for black dyes, and is also used for preserving timber. The solution is prepared for these purposes by dissolving partially rusted iron in crude vinegar; this liquid is therefore a mixture of ferrous and ferric acetates.

We have already explained the differences in constitution between the two classes of compounds, we have next to ascertain how far ferrous and ferric salts may be distinguished by chemical tests, and in making the following comparative experiments we shall employ the ferrous chloride solution prepared in Experiment 533

and preserved in a bottle containing iron wire, and the ferric chloride solution prepared in Experiment 534.

Experiment 544.—Take two test-tubes, half fill each with recently boiled distilled water,¹ to the contents of one tube add a few drops of ferrous chloride, to the other some ferric chloride; add to each solution of *potassium sulphocyanate*, $K'CNS$. Note that the ferrous solution is either unaltered by this addition or assumes a slight reddish colour, whereas the ferric solution becomes of a very deep *blood-red* colour, owing to the production of the strongly coloured ferric sulphocyanate, $Fe^{vi}_2(CNS)'_6$.

Experiment 545.—Proceed exactly as before, save that a few *drops* of *potassium ferricyanide*, $K_3Fe(CN)_6'''$, are added to the contents of each tube instead of the sulphocyanate. It is now the ferric salt that is unaffected or coloured only brown by the reagent, whereas a deep *blue* precipitate is formed in the ferrous solution. This blue precipitate is a variety of 'Prussian blue' named 'Turnbull's blue,' which is a potassio-ferrous ferrocyanide.

Experiment 546.—Make another comparison in a similar way with *potassium ferrocyanide*,² $K_4Fe(CN)_6^{iv}$, instead of the ferrocyanide. The reagent gives a *pale bluish* precipitate in the solution of ferrous salt, and a *deep blue* precipitate with the ferric compound.

¹ Thus freed from dissolved air, whose oxygen would change *some ferrous* into ferric salt.

² Commonly called 'yellow prussiate of potash'; the *ferricyanide* is distinguished as 'red prussiate of potash.'

Prussian Blue. Ferrous Carbonate. 187

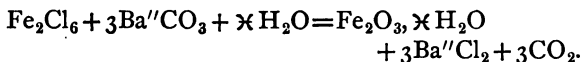
The dark blue precipitate formed in this experiment by the action of the ferrocyanide on the ferric salt is the ordinary variety of Prussian blue that is used as a pigment. It consists of $\text{Fe}_7\overline{\text{CN}}_{18}$.

Experiment 547.—Add potassium, sodium, or ammonium carbonate to the two iron solutions prepared as before. A *foxy red* precipitate is formed in the ferric solution consisting of a more or less hydrated ferric oxide, as a ferric carbonate does not seem to exist, while carbon dioxide gas is evolved. The ferrous salt affords a *greenish white* precipitate of ferrous carbonate, $\text{Fe}''\text{CO}_3$, which becomes dark green and ultimately brown when shaken up or exposed to air. This carbonate is met with in two pharmacopœial preparations, viz., the *mistura ferri composita*, B.P. ('Griffith's mixture'), where it is formed by the action of potassium carbonate on ferrous sulphate, and in the *ferri carbonas saccharata*, B.P., by the action of ammonium carbonate on ferrous sulphate. In the latter case the precipitate after washing with water is partially dried by pressure, and then rubbed with powdered sugar and dried. The sugar in some degree protects the ferrous carbonate from oxidation by the air.

Ferrous carbonate occurs in nature as the mineral *siderite*, or spathic iron, and when mixed with much earthy impurity as 'clay ironstone,' one of the most important ores of iron.

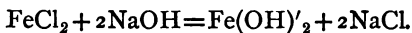
Experiment 548.—Instead of the soluble alkaline carbonate, add pure barium carbonate, previously rubbed in a mortar to the consistence of a thin

cream with water (in which it is insoluble), and note that no effect is produced in the case of the *ferrous* chloride solution, which is simply rendered turbid by the suspended barium carbonate ; but the *ferric* chloride is quickly decomposed without the aid of heat, a light foxy precipitate being formed and carbon dioxide gas evolved, while a portion of the barium dissolves as chloride. Add some more barium carbonate in order to ensure the presence of an excess, and then filter ; the filtrate should be colourless and quite free from iron, as indicated by the ferrocyanide test. Thus barium carbonate can completely separate iron from its solution. When the metal is in the ferric condition, the precipitate thus obtained consists of more or less hydrated ferric oxide ; thus :—



When iron in both conditions exists in solution as chlorides or nitrates (not sulphates), the metal in the ferric state can be completely precipitated by barium carbonate, leaving the ferrous compound still in solution.

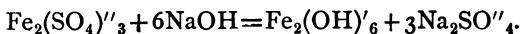
Experiment 549.—Add sodium or ammonium hydrate in excess to solution of a *ferrous* salt, and note that a nearly white precipitate is formed if the liquid is free from any ferric salt. The precipitate is ferrous hydrate, $\text{Fe}(\text{OH})'_2$, thus produced :—



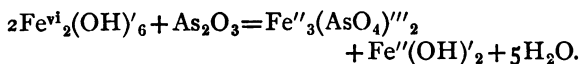
This precipitate quickly absorbs oxygen from the air,

and becomes green, and ultimately brown. When the hydrate is produced in an atmosphere of hydrogen, and dried and heated in the gas, nearly black ferrous oxide, FeO , results.

Experiment 550.—Add sodium hydrate (potassium or ammonium hydrates may be used instead) to solution of ferric sulphate until the mixture, after thorough agitation, is alkaline to test-paper. Note that a dark mahogany-coloured precipitate is formed; this is ferric hydrate thus produced :—



Pour the mixture on a filter and wash well with distilled water until the washings are no longer alkaline to test-paper. This moist precipitate is the *ferric peroxidum humidum*, B.P., which is used, as already stated¹ at p. 23, as an antidote for arsenic in the form of As_2O_3 . Its action as an antidote is partly mechanical and in part chemical; the latter depending on its power of converting the poison into the nearly insoluble and comparatively innocuous *ferrous arseniate* thus :—



Thus the arsenic is oxidised at the expense of the iron hydrate.

Ferric hydrate can be obtained in apparent solu-

¹ Ferric chloride solution may be precipitated instead, or, in a case of emergency, the 'muriatic tincture of iron.'

tion in water by a peculiar method which was discovered by the late Professor Graham.

Experiment 551.—To a moderately strong solution of ferric chloride, prepared as in Experiment 534, add fresh and moist ferric hydrate in small quantities at a time, and between each addition agitate well until solution is effected. In this way a comparatively large proportion of the hydrate can be dissolved. When further solution ceases filter the liquid. A very deep brown solution is thus obtained, which probably contains a ferric oxychloride or hydroxychloride.

Fig. 128.



This is to be poured into the glass vessel, marked A in fig. 128. This vessel (which may be half a wide-mouth bottle) has not a glass bottom, but a sheet of parchment paper¹ (*p*, fig. 128), secured by string, serves as the bottom on which the ferric chloride solution rests. A, which is termed a 'dialyser,' is slung, as shown, in a large vessel containing sufficient distilled water to cover the parchment paper of the apparatus; the volume of water should be fully twenty times that of the iron solution. Liquid diffusion now occurs through the parchment layer; the crystalline ferric chloride, Fe_2Cl_6 , passes through into the external water,

¹ Prepared by the action of a sixty per cent. sulphuric acid on unsized paper. This 'vegetable parchment' is easily purchased in good condition; but if any pin-holes occur in it the sheet must be dried and the hole stopped by touching the part with white of egg, and drying by the application of a hot iron.

while the uncrystalline ferric hydrate is left behind, but still in solution. The external liquid should be carefully replaced by fresh water every twenty-four hours ; and on the ninth or tenth day it will be found that little iron passes into the external water, while a species of solution of ferric hydrate remains in the dialyser. This is the *liquor ferri dialysati*, now much used in medicine. Minute traces of alkalies and of acids cause the rapid separation of the ferric hydrate as a somewhat gelatinous mass.

Experiment 552.—Dry some moist ferric hydrate at a temperature not exceeding 100° C., and powder the dry residue. Not only is the mere moisture of the pasty hydrate lost by this treatment, but some of the chemically combined water is driven off, and the compound left contains $\text{Fe}^{\text{I}}_2\text{O}''_2(\text{OH})'_2$. It is the *ferri peroxidum hydratum*, B.P. It is a reddish-brown powder, quite tasteless, and not attracted by the magnet. It dissolves completely, but slowly, when heated with diluted nitric acid.

Experiment 553.—Heat some of the dry hydrate in a crucible to dull redness ; all water is removed, and a dark red powder is obtained, which is ferric oxide, Fe_2O_3 . The ignited oxide is much less easily soluble in acids than any of its hydrates. Strong hydrochloric acid dissolves it on long digestion ; but it is more easily dissolved by boiling with sulphuric acid previously diluted with half its volume of water.

The best-marked native forms of ferric hydrates and oxides are the following, arranged in series, beginning with the normal hydrate :—

$\text{Fe}^{\text{I}}_2(\text{OH})'_6$.—Met with as the uncrystalline mineral *limnite* in stalactitic masses, or as a *yellow ochre*.

$\text{Fe}^{\text{I}}_2\text{O}''(\text{OH})'_4$.—*Limonite*, *brown hæmatite*, or *bog iron ore*.¹ When compact, of a dark brown colour, but often loose and porous in texture ; uncrystalline.

$\text{Fe}^{\text{I}}_2\text{O}''_2(\text{OH})'_2$.—*Göthite*,² a native crystalline hydrate, which occurs in striated prisms or tables.³

$\text{Fe}^{\text{I}}_2\text{O}''_3$.—*Specular iron ore*, met with in flattened rhombohedral crystals of black colour and brilliant metallic lustre. When the crystals are much flattened it appears as lustrous plates of *micaceous iron ore*. As *red hæmatite* it is fibrous or subcrystalline ; when mixed with much clay, sand, &c., it forms *red ochre*.

Ferric hydrate is easily soluble in many organic solutions—*e.g.* of sugar, citric or tartaric acids ; and it is remarkable that these solutions are not precipi-

¹ Bog iron ore is largely used in the purification of coal gas from sulphuretted hydrogen, which latter acts thus with ferric hydrate : $\text{H}_2\text{S} + \text{Fe}_2\text{O}(\text{OH})_4 = 2\text{Fe}(\text{OH})_2 + \text{S} + \text{H}_2\text{O}$.

² This hydrate is similar in composition to *manganite*. See p. 147.

³ The mineral *turgite* appears to be an uncrystalline compound of göthite with ferric oxide. It is probable that many specimens named turgite are mere mixtures of limonite or göthite with ferric oxide.

tated by an alkali when the latter is added in excess.¹ The alkaline liquids obtained afford in several cases uncrystalline varnish like layers on evaporation.

Experiment 554.—To a few crystals of citric acid, $\text{H}_3\text{Ci}'''$ ($=\text{H}_3\text{C}_6\text{H}_5\text{O}_7$), dissolved in water in a large test-tube, add moist ferric hydrate until the latter ceases to dissolve, even on heating; then make the liquid strongly alkaline with ammonium hydrate. If sufficient citric acid be present, a clear solution is obtained of a dark reddish-brown colour. Evaporate the liquid in a capsule until it assumes a syrupy consistence, then spread it in thin layers on glass plates, and dry completely at a very gentle heat in an oven. When dry, the residue can be scraped off the plates in deep red, easily soluble, *scales of ferri et ammoniæ citras*, B.P. This product is typical of many similar scale preparations² now used in medicine, and produced by analogous methods. The compound obtained as above is somewhat indefinite, but appears to be a salt of tribasic citric acid and approaching in composition to $\text{Fe}^{\text{v}}_2\text{O}_3(\text{NH}_4)_4\text{Ci}'''_2$.

Although ferric hydrate is not soluble in excess of sodium or potassium hydrate, save when organic matter is present, the general resemblance traceable between it and chromic hydrate, and between the

¹ This is a point of much analytical importance, as the presence of iron in a solution may be overlooked, owing to non-precipitation by excess of ammonium hydrate when organic bodies are present.

² *Ferrum tartaratum*, B.P., *ferri et quiniæ citras*, B.P., &c.

anhydrous oxides, leads us to anticipate that iron could afford *ferrites* analogous to the chromites (see p. 168), and we meet with such bodies in nature ; thus some pure specimens of the mineral *franklinite* approach to the formula $\text{Zn}''\text{Fe}^{\text{I}}_2\text{O}_4$,¹ or zinc ferrite, the zinc salt of a ferrous acid, $\text{H}_2\text{Fe}_2\text{O}_4$, whose representative among the iron hydrates is the mineral *göthite*, while the well-known and important mineral *magnetite*, or *magnetic iron ore*, is probably the iron salt of the same acid, $\text{Fe}''\text{Fe}^{\text{I}}_2\text{O}_4$. The composition of magnetic iron ore is commonly represented by the empirical formula Fe_3O_4 .² This does not give any real idea of the nature of the body, for it can be easily shown by the tests already given that the solution obtained by the action of hydrochloric acid on pure native magnetic oxide of iron contains the metal in the ferrous *and* ferric states. That being the case, it should be possible to effect the synthesis of magnetite in the following way :—

Experiment 555.—Weigh out nine grammes of ferrous sulphate ; dissolve *two-thirds* of it (*i.e.* six grammes) in about 50 c.cs of water, acidulate with sulphuric acid, and boil the solution with addition of enough nitric acid (as in Experiment 542) to completely convert the ferrous into ferric salt, then cool the liquid. Dissolve the remaining three grammes of unchanged ferrous sulphate in water and add the solution to that of the ferric sulphate just prepared ; mix well and add

¹ In most specimens a portion of the iron is replaced by Mn_2^{I} .

² Or $\text{FeO Fe}_2\text{O}_3$.

Synthesis of Magnetic Oxide of Iron. 195

immediately enough sodium hydrate solution to render the whole liquid alkaline after stirring thoroughly. Now boil the mixture for some time, when the dark precipitate produced becomes nearly black and more dense. Then catch the precipitate on a filter, wash it well with boiling water, and dry at about 70° C. The powder thus obtained is the *ferri oxidum magneticum*, B.P., and resembles the native magnetite in colour and in its most remarkable property—that of being *strongly attracted by a magnet*. As thus produced, however, it is hydrated, and contains about twenty per cent. of water. As already stated, it dissolves in hydrochloric acid and produces a liquid which gives the reactions of ferrous and ferric salt. A direct synthesis of the anhydrous compound was effected in Experiment 61.

Magnetic oxide of iron, or ferrous ferrite, is met with either massive or in the form of black sand—iron sand—the grains of which are often distinctly crystalline, the form being that of a regular octahedron. When the body is met with in quantity it forms a very valuable ore of iron. This ore sometimes contains small quantities of the element titanium (see p. 58). The question now arises, Can iron compounds be obtained analogous to manganates and chromates, and by similar methods? The experimental answer is thus obtained :

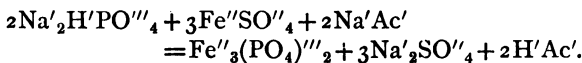
Experiment 556.—Make an intimate mixture of ferric oxide with one and a half time its weight of nitre, and heat the mixture to low redness in a tube of hard glass closed at one end. When the product

is cold, break the tube and throw the fragments into cold water; a somewhat purple liquid is then obtained, though much of the iron oxide remains undissolved. The colour of the solution is easily destroyed by heat, with evolution of oxygen and separation of ferric hydrate. The purple solution thus obtained has been shown to contain the compound K_2FeO_4 , which is obviously the analogue of potassium chromate, K_2CrO_4 , and potassium manganate, K_2MnO_4 . The salt is, then, potassium *ferrate*, doubtless derived from a ferric acid, H_2FeO_4 , which has not yet been isolated. As we have already seen, the alkaline ferrate is very unstable, like the manganate, but, unlike the latter, the ferrate wholly breaks up into ferric hydrate, caustic alkali, and oxygen, instead of passing on into a higher compound analogous to permanganate. Thus iron has less tendency to give rise to acidic oxidised radicles than manganese or chromium.

A hydrated ferrous phosphate is found in nature as the mineral *vivianite*, $Fe''_3(PO_4)'''_2 \cdot 8H_2O$. This is a dull blue compound, which is sometimes met with in monoclinic crystals. The synthesis of this body is easily effected.

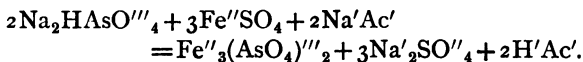
Experiment 557.— Dissolve some crystals of ferrous sulphate in water, and add solution of sodium hydrogen phosphate previously mixed with some sodium acetate, until no further precipitate is produced, shake thoroughly well and catch the precipitate on a filter, where it is to be washed with hot water and dried. The product is the *ferri phosphas*, B.P., and is a slate-blue amorphous powder, which is soluble in mineral acids, but is almost undissolved by acetic

acid ; hence the use of sodium acetate in its preparation. Sulphuric acid necessarily results from the action of $2\text{Na}_2\text{HPO}_4$ and 3FeSO_4 , and if allowed to remain in the liquid, would hold much ferrous phosphate in solution. When sodium acetate is present, however, it reacts at once with the sulphuric acid, sodium sulphate and free *acetic acid* resulting. The double reaction is expressed in the equation :—



The corresponding arseniate, *ferri arsenias*, B.P., is prepared by a precisely similar method.

Experiment 558.—Add a mixture of sodium hydrogen arseniate¹ and sodium acetate to solution of ferrous sulphate ; a greenish precipitate forms, which is washed thoroughly and dried. The arseniate is a green powder, readily dissolved by mineral acids, though only slightly soluble in acetic acid. The action of the sodium acetate is the same as in the last case.



We have already found (under Experiment 535) that sulphuretted hydrogen gas, when passed through a solution of ferric chloride, parts with its sulphur, which separates from the liquid as a yellowish-white

¹ In the directions of the Pharmacopœia the arseniate is to be dried at 300° F., in order to ensure definite strength, as the composition of the salt at that temperature is Na_2HAsO_4 .

body, while the hydrogen reduces the iron from the ferric to the ferrous condition ; but the iron is not precipitated as sulphide from the solution of ferrous salt by the excess of sulphuretted hydrogen so long as *free acid* is present.

Experiment 559.—Add some ammonium sulphhydrate to a solution of pure ferrous sulphate. Note that a black precipitate forms immediately, and is not dissolved by excess of the reagent. This precipitate consists of ferrous sulphide, FeS , which is easily soluble in dilute acids. When the precipitate is thrown on a filter and washed with water, it gradually becomes brownish, owing to oxidation.

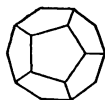
The sulphide thus obtained is the hydrated form of the body we have already produced by the direct union of its elements, under Experiment 273, for use in the preparation of sulphuretted hydrogen. This sulphide is only met with in meteorites as the mineral *troilite*.

The sulphide Fe_2S_3 , corresponding to ferric oxide, does not occur in the free state in nature, but is produced by heating a mixture of two atoms of iron with three of sulphur. Like ferric oxide, it can act a somewhat acidic part and unite with monosulphides as with cuprous sulphide, Cu_2S , to form the compound $\text{Cu}''_2\text{Fe}_2\text{S}_4$, or 'copper pyrites,' which is thus a cuprous sulphoferrite. With ferrous sulphide it also unites to form a body termed 'magnetic pyrites,' which is found native, and which should consist of $\text{Fe}''\text{Fe}^{\text{I}}_2\text{S}_4$, if it conformed to the type of magnetic oxide of iron $\text{Fe}''\text{Fe}^{\text{I}}_2\text{O}_4$; but the analyses of native specimens lead to the formula $\text{Fe}''\text{Fe}^{\text{I}}_2\text{S}_4$.

4FeS , or 5FeS . The facility with which the ferrous sulphoferrite unites with additional FeS is doubtless due to the easy development of the tetratomic character of some of the sulphur atoms present. As its name implies, this peculiar sulphide is magnetic, like the oxide to which it seems most closely related.

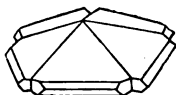
When ferrous sulphide is powdered and very carefully heated with another atom of sulphur, a compound is obtained which is not magnetic, and is identical in composition with common 'iron pyrites,' FeS_2 . This disulphide is met with in nature in two distinct forms, which exhibit high metallic lustre: (1) *cubical pyrites*, in pale yellow crystals, which are either cubes or the closely related form of the same system, termed *pyritohedron* (see fig. 129), and in granular masses. This variety of pyrites is hard, varying in degree of hardness from 6° to 6.5° . Its specific gravity

FIG. 129.



is about 5 (water = 1); it is very slowly oxidised by exposure to air at ordinary temperature, though it easily suffers the decomposition referred to under Experiment 303 (see Part II., p. 228); (2) *Cockscomb pyrites*, or *marcasite*, which is of a *pale bronze-yellow colour*, and occurs in flattened trimetric crystals, like fig.

FIG. 130.



130, often arranged in groups of crest-like form: hence the term *cockscomb*. The hardness of this variety is also from 6° to 6.5° ; but its specific gravity is less—about 4.8. This is the form of pyrites usually found in coal (and sometimes

mistaken for gold, owing to its colour). It oxidises in moist air much more rapidly than the ordinary or cubical pyrites, affording ferrous sulphate and sulphuric acid (see p. 182).

The physical distinctions between the two forms of iron disulphide obviously *may* be due to difference in structure of the chemical molecule, though no such difference has yet been distinctly traced. If either molecule be correctly represented by the formula FeS_2 or $\text{S}'=\text{Fe}^{\text{iv}}=\text{S}''$, and not by some multiple of it, the compound is to be regarded as the sulphur representative of the unknown oxide FeO_2 .

An iron arsenide is known, termed *leucopyrite*—in allusion to its white colour—whose formula is FeAs_2 , and an arsenio-sulphide termed *mispickel*,¹ or arsenical pyrites, occur in comparatively large quantities. These minerals crystallise in the same system as the marcasite variety of iron pyrites, and all three bodies are found to graduate into one another; hence they are probably also similar in chemical structure. Now the simplest representation of the mispickel molecule, having regard to the atomicities of its constituents, is the following: $\text{Fe}_2\text{As}_2\text{S}_2$, or—



Then by analogy leucopyrite should be written Fe_2As_4 and marcasite Fe_2S_4 , or 2FeS_2 . This view is strengthened by the composition of a mispickel analogue termed *glauco-dote*. This mineral crystallises in the same system and conforms to the mispickel type, but

¹ Used as a source of arsenic in Experiment 35A.

has two-thirds of *two* atoms of iron replaced by the metal *cobalt*, which is isomorphous with iron.

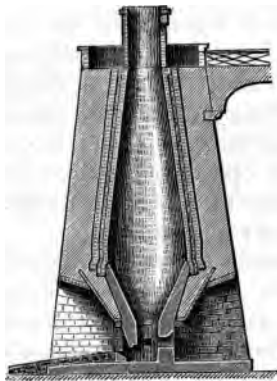
Iron is met with in commerce in three principal forms, viz., *pig* or *cast iron*, *wrought iron*, and *steel*. The order in which these forms of the metal are mentioned is also the order of manufacture, for cast iron is almost invariably the immediate product from the ore, while wrought iron and steel are produced directly or indirectly from the pig. Although the manufacture of iron is one of the most important of our industries, the metallurgical operations involved are simple *in principle*, and by no means so complicated in practical details as those of copper smelting.

Cast iron is the direct product from the minerals used, and the *first stage* of the process aims at bringing the iron in the ore to the state of oxide. The ores worked are clay ironstone—impure ferrous carbonate—red hæmatite and magnetic oxide; these are slowly roasted in great heaps, consisting of the broken ore and refuse coal. Moisture is thus driven off and carbon dioxide, while the residue consists essentially of a mixture of ferric oxide and silicates of various kinds.

In the *second stage* of the treatment, the roasted ore is reduced to metallic iron; the latter, which is very difficult of fusion, is then made to unite with about four per cent. of carbon which greatly increases its fusibility, while the silicates are removed by the aid of lime as fusible slag. The process is conducted in a furnace, similar to that shown in section at fig. 131. A mixture of roasted ore, limestone and coal is supplied at the top of the conical furnace, the hot and but par-

tially oxidised gases arising from which readily reduce the ferric oxide of the ore to metal ; as the mass subsides into the hotter parts of the furnace, the lime

FIG. 131.



comes into play as a 'flux,' for it attacks the earthy silicates in the ore and forms therewith an easily fusible slag, consisting chiefly of silicates of calcium, aluminum, and some iron; this falls to the bottom of the furnace and is drawn off. The spongy reduced iron is thus exposed at a very high temperature to the action of white-hot carbon, with which it then readily unites, and the

easily fused product falls on the furnace hearth, from which it is drawn off and cast in oblong moulds ; out of these it is turned when cold, as the pig or ingot of cast iron. The iron furnaces work continuously for many months.

Cast iron contains, as already stated, about four per cent. of carbon, a little silicon, and traces of sulphur and phosphorus ; the two latter impurities greatly affect the quality and therefore the value of the metal. Cast iron when fractured is seen to be distinctly crystalline in structure, hence it is brittle and deficient in tenacity. If white in colour, most of its *carbon is in combination* as a feeble carbide of iron ; *but if grey, plates of graphite can be detected im-*

bedded in the crystalline material which still contains some of the carbon in combination.

Wrought iron is produced from pig iron by a process termed 'puddling,' the object in view being the removal of all the silicon and most of the carbon

along with sulphur and phosphorus. The process is one of oxidation, and is carried out in a furnace of the form shown in fig. 132, where the flame, arising

FIG. 132.



from the fuel at F, is made to play on a mass of cast iron placed on the bed A. When the pigs have melted, air is admitted which burns the carbon of the iron and forms CO and CO₂ gases, which pass off; the silicon also oxidises and forms a fusible silicate of iron, which separates as a slag, in which most of the sulphur and phosphorus¹ originally present are also found. As the carbon is burned out of the iron, the latter becomes less fusible, and a workman introduces a long iron rod through the side-door D in the furnace, and stirs up or 'puddles' the now pasty mass so as to facilitate the oxidation. When the process is com-

¹ A very little sulphur makes the iron crack under a blow when hot. The metal is then technically said to be *red short*. Phosphorus makes it *cold short*, i.e. cracks under a blow when cold.

plete, red hot balls are removed and rolled or pressed, so as to weld the particles of iron and squeeze out adherent slag. The product is wrought iron. This differs from cast iron in being nearly pure, and in possessing a fibrous structure, toughness and tenacity: consequently it is easily drawn into fine wire.

Steel is almost intermediate in proportion of carbon between cast and wrought iron. The latter is superficially converted into steel by heating bars or plates imbedded in charcoal; the iron unites with some carbon and is superficially converted into steel, which is granular and possesses the highly important property of becoming exceedingly hard when suddenly cooled from a high temperature. Wrought iron thus converted into steel can be fused and cast. The product is *cast steel*.

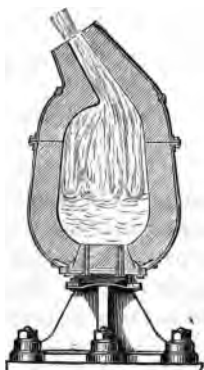
The following table contains the results of analyses of specimens of cast iron, wrought iron, and steel. The total carbon only is given in each case :—

	Cast	Wrought	Steel.
Iron . .	92·2	99·24	98·57
Carbon . .	3·5	0·30	1·20
Silicon . .	2·6	0·13	0·03
Sulphur . .	0·3	0·12	traces.
Phosphorus . .	0·6	0·11	traces.
Manganese . .	0·8	0·30	0·20

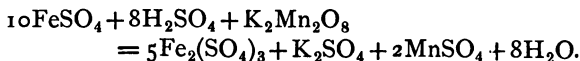
Such a comparison may suggest the idea that a suitable mixture of cast iron with wrought iron should, if fused *together*, afford steel on casting; and this is substantially *the principle* involved in the now celebrated process

of Sir Henry Bessemer, F.R.S. The operations are conducted in a large iron vessel lined with highly refractory clay; this vessel, which is termed a Bessemer 'converter,' is shown in section in fig. 133. It is charged with a quantity of molten cast iron, and a stream of hot air is blown through the liquid metal. The effect is to burn out the carbon and silicon, and the temperature resulting from this combustion is high enough to maintain the nearly pure iron in the molten state. When this point has been reached sufficient of a white cast iron, termed 'Spiegeleisen,'¹ is added to bring up the percentage of carbon in the whole mass to the steel standard. After again turning on the air blast to effect mixture, the product is cast and forms Bessemer steel.

FIG. 133.



Note.—In quantitative analysis potassium permanganate is often used for the conversion of ferrous into ferric salts. It reacts thus on ferrous sulphate in presence of free sulphuric acid:—



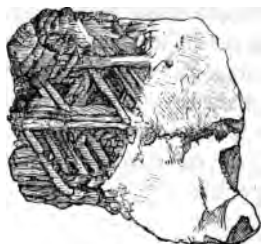
¹ Spiegeleisen contains about five per cent. of carbon and six per cent. of *manganese*. The latter is believed to improve the quality of the steel.

CHAPTER XXXIX.

EXPERIMENTS WITH COBALT AND NICKEL
COMPOUNDS.

THE fact was pointed out at the beginning of the last chapter that the iron met with in meteoric masses is in part alloyed with another metal, named *nickel*, together with a little *cobalt*. This alloy is crystalline, and is easily distinguished when a polished surface of meteoric iron is acted upon by very dilute hydrochloric acid ; the pure iron dissolves, while the alloy

FIG. 134.



of iron with nickel is not materially affected : hence a pattern¹ is developed which is produced by interlaced crystals of the alloy. The appearance of the etched surface is well shown in the annexed drawing from a piece of meteoric iron which fell at Xiquipilco,

in Mexico, to be seen in the Natural History Museum, Dublin. Thus metallic iron, nickel, and cobalt are closely associated in nature.

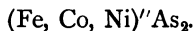
Again, an arsenide of nickel is known named

¹ Termed Widmannstätten pattern.

rammelsbergite,¹ which resembles leucopyrite in crystalline form, and, like it, is a diarsenide, NiAs_2 , or Ni_2As_4 , while another mineral termed *nickel glance*, or *gersdorffite*, consists of NiAsS or $\text{Ni}_2\text{As}_2\text{S}_2$, and is the chemical analogue of mispickel, though it crystallises in a form of the monometric system ; moreover, in specimens of these minerals, iron often replaces a portion of the nickel. Thus some at least of the native compounds of nickel and iron are closely related.

At the end of the last chapter it was pointed out that iron is associated with cobalt in the mineral *glauco-dote*. This body is a mispickel with part of the iron replaced by cobalt, while *cobalt glance*, or 'silver white cobalt ore,' is the arsenio-sulphide of cobalt only. *Smaltine*, or grey cobalt, is the corresponding simple diarsenide CoAs_2 or Co_2As_4 .

Finally, all these metals² are present in the mineral *eisencobaltnickelerz*, which is a compound formed on the chemical type of leucopyrite. When cobalt predominates, the mineral is termed 'speiss cobalt.' The formula for the compound is usually written—



The symbols thus written within brackets in this expression and in similar mineralogical formulæ do not represent single atoms of the elements, but only indicate the bodies by which the chief metal—in this

¹ *Cloanthite*, or white nickel, has the same composition, but it assumes crystalline forms of the monometric or cubic system.

² It is well to add here that the three metals are not only associated in nature, but agree in possessing the magnetic property strongly marked.

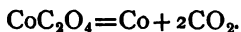
case iron—suffers equivalent substitution, in accordance with Mitscherlich's law (see p. 13).

. It is thus obvious that the study of cobalt and nickel should follow that of their natural associate, iron.

COBALT, $\text{Co}^{\text{iv}}=58.6$.—Metallic cobalt is not met with in the free state in nature, save in the meteoric mixture already noted. Its principal ores are the arsenides and arsenio-sulphides just referred to. It is also met with as rosy arseniate in 'cobalt bloom,' and as an oxide along with manganese in black cobalt ore; but since the chief minerals usually contain nickel and iron, as well as cobalt, it will be convenient to reserve our outline of their metallurgical treatment for the end of this chapter (see p. 220). The compound of cobalt that can be most easily obtained by the student is the nitrate, a fine rosy-red coloured salt, which is deliquescent and very easily soluble in water. It is obtained by the solution of an oxide or carbonate of the metal in nitric acid, and the crystals contain $\text{Co}''(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. From this beautiful salt the metal and most of its compounds can be prepared by the methods given in the following experiments:—

Experiment 560.—Add to solution of cobalt nitrate sufficient potassium *oxalate* to completely precipitate the cobalt as oxalate, $\text{Co}''\text{C}_2\text{O}'_4$. Collect the precipitate, wash it with water, and dry it. Now place some of this powder in a porcelain crucible provided with a good cover, and heat, at first gradually, *but after some time very strongly*, over the Bunsen flame. Gas is evolved, which is carbon dioxide, and

the residue left in the crucible is metallic cobalt in a fine state of division. The oxalate is thus decomposed :—



The powder is attracted by a magnet ; when rubbed, it exhibits metallic lustre and is grey in colour. The metal requires nearly as high a temperature for fusion as iron. Its specific gravity is about 8.7. Cobalt dissolves in hydrochloric and in nitric acid with the aid of heat, and affords the corresponding salts of the metal.

Experiment 561.—Add to a dilute solution of cobalt nitrate, which is of a rosy colour, sodium hydrate. Note that a blue precipitate is formed which is a basic nitrate, and insoluble in excess. It becomes greenish on exposure to the air. If, however, the mixture be heated to boiling, the precipitate changes to pale red, and then consists of the hydrate $\text{Co}''(\text{OH})'_2$. This body soon becomes brownish, owing to absorption of oxygen from the air and production of a higher oxide.

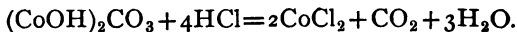
When the hydrate is dried and carefully heated to low redness in a current of carbon dioxide gas, a greenish powder is obtained, which is the oxide CoO . This is reduced to metallic cobalt when heated in an atmosphere of hydrogen, and the metal thus obtained is pyrophoric, like iron (see Experiment 52).

Experiment 562.—Add ammonium hydrate in excess to cobalt nitrate solution, and note that a pre-

precipitate forms as before, but easily redissolves in excess, and produces a reddish-brown liquid.¹

Experiment 563.—Add sodium carbonate in excess to a solution of cobalt nitrate, and note that a violet-blue precipitate is formed. This is a basic carbonate, in part consisting of $(\text{CoOH})'_2\text{CO}_3$. If, however, a solution of sodium hydrogen carbonate, (NaHCO_3) , or 'bicarbonate of soda,' charged with carbon dioxide, be used, instead of the carbonate Na_2CO_3 , and the mixture heated under pressure, a red precipitate is obtained, which contains the compound CoCO_3 . Barium carbonate shaken up with solution of cobalt nitrate or chloride does not precipitate the metal.

Experiment 564.—Collect the *basic* cobalt carbonate obtained in the last experiment on a filter, wash it well with water, and pour over the precipitate diluted hydrochloric acid. The precipitate dissolves and a liquid passes through the filter which contains the chloride CoCl_2 , and even affords crystals of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$.



Cobalt sulphate can be obtained in a similar way by dissolving the carbonate in dilute sulphuric acid, or by heating crystals of the nitrate with strong sulphuric acid until no more nitric acid is evolved. The product when cold is diluted with water and the solution slowly crystallised, then crystals of the salt

¹ Cobalt affords with ammonia a large number of compounds of complex constitution, the study of which the student should reserve for his advanced course.

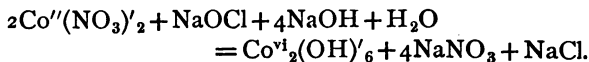
separate, consisting of $\text{CoSO}_4, 7\text{H}_2\text{O}$. This body not only contains the same number of molecules of water of crystallisation as ferrous sulphate, but is isomorphous with the latter body. Cobalt sulphate is found native in small quantity as the mineral *bieberite*.

Experiment 565.—Paint a sheet of white paper with a rather dilute solution of cobalt nitrate or chloride, preferably the latter ; or write with the solution as ink. While moist the paper is of a rosy tint, and the tracing is almost invisible ; but if held before the fire for a short time, so as to dry thoroughly, the colour changes to *blue*, and the tracing is easily seen. When the blue paper is brought into a damp atmosphere or breathed upon, the rosy colour is restored. The colour changes noted obviously depend on hydration, and it is usually found that the hydrated cobalt salts are red, while the anhydrous compounds are blue. Paper coloured with cobalt salt has long been sold as a weather-indicator, for it is rosy when the atmosphere is highly charged with moisture, and rain is therefore near, but blue in dry weather. As already indicated, a cobalt solution may be used as a secret or *sympathetic* ink, as characters written with it are almost invisible, and remain so until the paper is heated.

Unlike ferrous salts the corresponding cobalt compounds are not affected by boiling with nitric acid, but a body corresponding to the ferric hydrate $\text{Fe}_2(\text{OH})_6$ can be obtained thus :—

Experiment 566.—Add to a solution of cobalt nitrate or chloride excess of sodium or potassium hypochlorite, NaOCl or KOCl (see Experiment 151), containing some free alkali. A precipitate forms

which is nearly black. This consists of cobaltic hydrate, $\text{Co}^{\text{vi}}_2(\text{OH})'_6$, and its production may be explained by the following equation :—¹



The production of a hydrate of this order is evidence of the *tetrad* character of cobalt, as in the analogous case of iron.

When gently heated the hydrate is converted into Co_2O_3 , or cobaltic oxide.

The hydrate dissolves in cold hydrochloric acid and forms a brown solution, which contains a very unstable *cobaltic* chloride, Co_2Cl_6 . This body easily decomposes, even in the cold, into chlorine and the stable *cobaltous* chloride, thus :—



In this respect cobalt resembles manganese more than iron.

Experiment 567.—Heat strongly a few crystals of cobalt nitrate in a porcelain crucible. Note that nitrous fumes are evolved and a black residue is ultimately obtained. This product is an oxide analogous to magnetic oxide of iron in composition, and is

¹ An interesting mode of obtaining oxygen gas may be here mentioned. Take a solution of bleaching lime and add to it a few drops of cobalt nitrate solution. The above black cobaltic hydrate separates, but oxygen gas is steadily evolved from the liquid until the whole of the oxygen is separated from the hypochlorite present. A very small proportion of cobaltic hydrate serves to set up this change and complete it.

represented by the formula Co_3O_4 . This black oxide of cobalt is probably saline in structure like its iron analogue, and should be thus written : $\text{Co}''\text{Co}_2\text{O}''_4$. A native sulphide analogous to this oxide exists : it contains $\text{Co}, \text{Co}_2\text{S}_4$; its name is *linneite*, or cobalt pyrites. The black oxide is used in the arts for colouring glass of a fine *blue* tint.

Experiment 568.—Support on a loop of platinum wire a few small fragments of broken glass, and fuse in the blowpipe flame (see under Experiment 264). When fused add to the bead a minute particle of the black oxide of cobalt just prepared, and again fuse.¹ Note that a rich *blue* colour is produced, which remains on cooling.

Cobalt blue or *smalt*, which is used as a pigment, is a potassium glass containing cobalt silicate. Potassium carbonate and excess of sand are fused together and a crude cobalt oxide added to the molten mass ; when the oxide is dissolved and the resulting cobalt silicate diffused through the glass, the latter is cooled, broken up, and ground to fine powder. The depth of tint varies with the proportion of cobalt present, but the latter rarely exceeds 14 per cent.

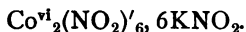
Another cobalt blue, termed *Thenard's blue*, and a *cobalt green* will be produced later on.²

A *cobalt yellow* can also be thus obtained ; but its formation is of more analytical than technical importance.

¹ Instead of glass the borax bead may be used, as in Experiment 321.

² For Thenard's blue see p. 228, and for the green see p. 241.

Experiment 569.—Acidulate a solution of cobaltous chloride with *acetic acid* and add to the liquid potassium *nitrite* in solution; a yellow precipitate forms, which can be collected, washed, and dried. It is slightly soluble in water, but insoluble in alcohol. This body may be regarded as a more or less hydrated compound of cobaltic nitrite with potassium nitrite, in the proportions indicated by the formula—



It is often termed ‘Fischer’s salt,’ after its discoverer, and is used to separate cobalt from solutions of the metal containing nickel, iron, &c., as these elements are not precipitated under the conditions. The yellow cobalt compound is dissolved on heating with hydrochloric acid, and is decomposed at the same time, cobaltous and potassium chlorides resulting.

We have already dealt in some detail with the native sulphides and arsenides of cobalt, but have not yet produced cobaltous sulphide artificially.

Experiment 570.—Pass a current of sulphuretted hydrogen gas through a solution of cobaltous chloride containing free hydrochloric acid. No precipitate forms even on heating the liquid. Now boil in order to expel all trace of H_2S , and, when cool, add to the liquid excess of ammonium hydrate: the latter, as in Experiment 562, redissolves the precipitate of cobaltous hydrate it first produces; and if we now pass sulphuretted hydrogen through this *alkaline* liquid,¹ a black precipitate is formed, consisting of

¹ Or add ammonium sulphhydrate instead of passing the gas.

the hydrate of CoS .¹ This body is not soluble in excess of alkaline sulphide. Catch the precipitate on a filter, wash well with water, and then pour over it cold dilute hydrochloric acid. The acid has little apparent effect upon the sulphide, whereas if the acid be hot and moderately strong, cobaltous sulphide dissolves.

NICKEL, $\text{Ni}=58.6$.—The nearest approach to free nickel met with in nature is in the meteoric alloy already referred to.² In addition to the arsenides and arsenio-sulphides of nickel, rammelsbergite, cloanthite, and gersdorffite, noticed at the beginning of the chapter, nickel forms a pale copper-coloured native arsenide, termed *kupfernickel*, or 'copper nickel' (in allusion to its colour), which has no analogue amongst the cobalt or iron compounds, since its composition is NiAs , or Ni_2As_2 . This is one of the chief ores of the metal, and its metallurgical treatment will be noticed later on. A silicate of nickel has recently been discovered in New Caledonia, which is now being worked for metal in Birmingham. Metallic nickel is an article of commerce, and can be easily purchased in a tolerably pure condition. The metal is nearly silver white, hard, and susceptible of a good polish, which it retains, as it does not quickly oxidise, or rust. Its specific gravity is 8.9. It is magnetic, like iron and cobalt. It is rather more fusible than iron, and can be rolled into plates and drawn into wire. *German*

¹ Met with in nature as the mineral *seyppoorite*.

² A phosphide of nickel, termed *schreibersite*, is often met with in meteoric masses.

silver is an alloy of nickel with copper and zinc, which contains in 100 parts:—

Nickel	20
Zinc	20
Copper	60

The 'white metal,' which is the usual foundation for silver-plating, is similar to the above in composition, but contains less nickel and more zinc.

Nickel is now largely employed for plating iron articles, the metal being deposited from solution by electricity, as in silver-plating.

Experiment 571.—Pour some diluted sulphuric acid into a beaker, add fragments of metallic nickel, and heat. The metal dissolves,¹ while hydrogen gas is evolved. When action ceases, filter the liquid from excess of metal into a porcelain capsule and evaporate the *green* solution thus obtained. On cooling, bright green crystals separate, which consist of $\text{NiSO}_4, 7\text{H}_2\text{O}$.² This body is isomorphous with ferrous sulphate. Nickel chloride, NiCl_2 , and nitrate, $\text{Ni}(\text{NO}_3)_2$, are easily obtained as above by dissolving the metal in the suitable acid. From any of these solutions nickel oxalate, NiC_2O_4 , may be precipitated, as in the case of cobalt, and similarly reduced to metal by ignition out of contact with air.

Experiment 572.—Add sodium hydrate to solu-

¹ It is also soluble in diluted hydrochloric and nitric acids.

² When solution of ammonium sulphate is added in excess to a saturated solution of nickel sulphate, a crystalline body separates, which contains $\text{NiSO}_4, (\text{NH}_4)_2\text{SO}_4, 6\text{H}_2\text{O}$.

tion of nickel sulphate, and note that an apple-green precipitate is formed. This body is nickel hydrate, $\text{Ni}''(\text{OH})_2$, and is insoluble in excess of sodium or potassium hydrates. Unlike the corresponding cobalt compound, this body does not tend to absorb oxygen, and when very strongly heated parts with water, while nickel oxide, NiO , remains as a greyish-green powder.

Experiment 573.—Add some ammonium hydrate to solution of nickel sulphate, and note that the hydrate first precipitated redissolves in excess to a bluish solution, which latter on boiling off the ammonia deposits some nickel hydrate.

Experiment 574.—Add sodium carbonate in excess to solution of nickel sulphate, and note that a green precipitate is produced. This is a basic carbonate, which approaches in composition to the analogous cobalt compound, and in part contains $(\text{NiOH})_2\text{CO}_3$. The normal carbonate can be obtained by a method similar to that given under Experiment 563. Barium carbonate shaken up with solution of the nitrate or chloride does not precipitate the nickel.

Experiment 575.—Repeat Experiment 566, using nickel sulphate and alkaline hypochlorite. As in the case of cobalt, a black precipitate forms, and this consists of $\text{Ni}^{\text{VI}}_2(\text{OH})_6$. When this is collected, dried, and carefully heated, it can afford the oxide Ni_2O_3 , which latter is a black powder. The sesquioxide affords NiO on strong ignition. When either oxide or hydrate is dissolved in hydrochloric acid, chlorine is evolved, and the chloride NiCl_2 results.

The sesquioxide and its hydrate afford evidence of the *tetrad* character of nickel, but no salts are yet

definitely known in which this metal so acts, as the compounds analogous to Mn_2Cl_6 , Cr_2Cl_6 , Fe_2Cl_6 , or Co_2Cl_6 are wanting. Moreover, no compounds have yet been obtained in which nickel plays an acidic part, as manganese does in the manganates and permanganates. Nor does nickel afford an oxide of the composition Ni_3O_4 .

Nickel is not precipitated by potassium nitrite.

Experiment 576.—Touch a borax bead with any nickel compound and fuse, nickel oxide dissolves and a glass is formed, which, when hot, is violet if heated in the outer flame of the blowpipe, but grey or brownish in the inner flame.

Experiment 577.—Repeat Experiment 570, using nickel sulphate, and note that while sulphuretted hydrogen fails to precipitate nickel from solution acidulated with hydrochloric acid, it affords a black precipitate in *alkaline* solution on addition of sulphuretted hydrogen, or alkaline sulphhydrate. This precipitate consists of a hydrate of NiS ,¹ which is not altogether insoluble in excess of ammonium sulphhydrate, particularly if free ammonia be present, and the solution in alkaline sulphhydrate has a *brown* colour. Nickel sulphide, like that of cobalt, is very slightly soluble in cold hydrochloric acid, though soluble in boiling acid.

The action of potassium cyanide, KCN , in solutions of the two metals cobalt and nickel, serves such important purposes in analysis that we cannot omit the following experiments, though junior students

¹ *This sulphide is found native as 'hair nickel,' or millerite,*

are not advised to repeat them, except under careful supervision, as the reagent to be employed is a *deadly poison*, and its use should be avoided whenever possible.

Experiment 578.—To a neutral solution of cobalt nitrate add potassium cyanide, also in solution. Note that a precipitate first forms of a brownish-white colour, but this easily dissolves in excess of cyanide. Then boil the liquid for some minutes and allow it to cool. To a portion (*a*) add a few drops of diluted hydrochloric acid, taking care to hold the vessel under a flue with a good draught, as some *prussic* or hydrocyanic acid is evolved. No precipitate is produced. To another portion (*b*) add solution of sodium hypochlorite. No precipitate is produced in this case either.

Experiment 579.—Make a similar experiment with nickel sulphate solution, and note that (*a*) when diluted hydrochloric is added a yellowish-green precipitate is obtained, which consists of nickel cyanide, $\text{Ni}''(\text{CN})'_2$, and (*b*) when a portion of the liquid is treated with solution of sodium hypochlorite a *black* precipitate is formed, which consists of the hydrate $\text{Ni}_2(\text{OH})_6$.

When potassium cyanide is added to cobalt or nickel solution the cyanides of the metals are precipitated, *i.e.* $\text{Co}''(\text{CN})_2$ or $\text{Ni}''(\text{CN})_2$, but redissolved by excess of the reagent, with the production of soluble double cyanides. In the case of nickel the compound $\text{Ni}(\text{CN})_2 + 2\text{KCN}$ results, and this is not altered by boiling. If the solution be acidulated the solvent, potassium cyanide, is decomposed and the

nickel cyanide it previously held in solution is precipitated, while the double cyanide reacts like any other soluble nickel salt with a hypochlorite. Cobalt forms a similar double cyanide to that of nickel *in the cold*, and then reacts like the latter ; but on boiling a new body is formed, termed potassium cobalticyanide, $K_3Co(CN)_6$, which is not affected by acid or hypochlorite.

Extraction of nickel and cobalt.—The two metals usually occur together in the ores, combined with arsenic and sulphur, and mixed with more or less iron and copper. The first step in the treatment of these ores and of kupfernicksel is that of roasting, whereby much sulphur and some arsenic are oxidised and driven off, while the residue, when fused, affords a species of slag or *matt*, which contains much iron with copper and sulphur, and floats on a heavy metal-like material termed *spieß*, which contains nickel, cobalt, and arsenic. The next stage is that of roasting the *spieß*, whereby most of the arsenic is driven off, and the residue is a mixture of crude metallic oxides. These are then dissolved in hydrochloric acid and sufficient bleaching lime added to convert the iron present into ferric oxychloride, which precipitates and carries with it any arsenic present. The remaining solution is treated with sulphuretted hydrogen to precipitate copper and lead, and the liquid, which now contains only cobalt and nickel, is treated with a further quantity of bleaching lime, previously ascertained by analysis to be necessary to precipitate the whole of the cobalt as *cobaltic hydrate*, without affecting the nickel, which *latter* is separated as hydrate, after removal of cobalt,

by addition of milk of lime. The nickel hydrate is then reduced to metal by heating with carbon. The cobaltic hydrate can be either reduced to metal by heating with carbon, or converted into *smalt* or *cobalt blue* by fusion with siliceous sand and potassium carbonate. The cobaltic hydrate is also used in the manufacture of *cobalt green*¹ (Rinemann's) and *cobalt ultramarine*.²

¹ See ZINC.

² See ALUMINUM.

CHAPTER XL.

EXPERIMENTS WITH ALUMINUM COMPOUNDS.

ALUMINUM, $Al^{iv}=27\cdot3$.—Most specimens of crude red or brown hematite and of clay ironstone afford on analysis varying proportions of an oxide of the metal *aluminum*. This oxide, termed *alumina*, is a common associate of ferric oxide in nature ; in most cases the iron compound predominates, but there are numerous hydrated transition minerals between the aluminous hæmatites and more or less ferruginous ‘alum clays.’ Amongst the latter the best known is *bauxite*, which is met with as concretionary grains in limestone at Baux (or Beaux), near Arles, in France, but a mineral of much higher purity is obtained in large quantity near Glenarm, County Antrim, in Ireland, and the latter is now chiefly used as a source of aluminum compounds. The following are comparative analyses of bauxite and the best Irish alum clay.

	Bauxite	Alum Clay
Alumina . . .	53·4	65·0
Ferric oxide . .	27·0	0·5
Silica	2·5	4·5
Water combined .	17·1	30·0
	<hr/>	<hr/>
	100·0	100·0

Thus the Irish alum clay, unlike bauxite, contains but traces of iron ; the small quantity of silica in it is

probably present as hydrated aluminum silicate, and the residue is a nearly pure aluminum hydrate. Such a mixture is not correctly named 'clay,' as the term is generally applied to an aluminum silicate, which is met with either as the beautiful white *kaolin*, or 'china clay,' or, in a very impure mixture, in the common soil of the garden and the field.

All aluminum compounds and the metal itself are derived either from bauxite, Irish alum clay, or kaolin, of varying degrees of purity, and the student can best commence his experiments with either of the two latter bodies, as they are easily purchased in excellent condition and almost quite free from iron.

Experiment 580.—Mix pure white kaolin, or porcelain clay, with about half its weight of oil of vitriol in a capsule. If Irish alum clay be used, its own weight of strong sulphuric acid may be employed. Mix the powder with the acid and heat for some time to about 100° C., with occasional stirring, but take care to avoid 'spiriting' through over-heating. When combination has taken place, allow the mass to cool,¹ then add about six times its weight of water, mix well, boil and filter. An acid liquid, having a sweetish astringent taste, passes through, and a residue is left on the filter which contains the silica of the clay, if kaolin was used in the first instance. Now evaporate the filtered liquid down to a syrupy consistence and allow it to

¹ The nearly solid mass obtained is the *alum cake* used by paper makers in resin and other sizing. It is also used as a mordant in dyeing (see p. 228), and as a precipitant for sewage. In the latter case it is prepared from crude brick clay.

cool, when crystalline crusts separate. These are found on analysis to consist of hydrated aluminum sulphate, and the formula of the compound is $\text{Al}_2(\text{SO}_4)''_3, 16\text{H}_2\text{O}$, if the atomic weight of aluminum be 27.3 and the heat capacity of the element accords with this value. This sulphate is obviously analogous to ferric sulphate as the two aluminum atoms seem to form a hexad pair like Fe^{VI}_2 : we therefore infer that each aluminum atom is *tetrad*, and the composition of the chloride (see p. 231) and other compounds support this view. Analogical reasoning would lead us further to expect the existence of compounds whose molecules contain but one atom of aluminum acting as a diad, like iron in ferrous salts, or as a tetrad like manganese in some of its compounds, *but no such bodies are yet known to exist.*¹

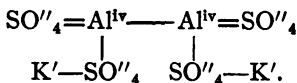
Aluminum sulphate forms a very remarkable group of addition compounds, named *alums*, which are alike in constitution, crystalline form, and hydration, since all contain twenty-four molecules of water.

Experiment 581.—To the solution of aluminum sulphate obtained as above, but diluted with a little water so as to dissolve the crystals, add potassium sulphate equal in weight to about two-thirds of the sulphuric acid originally used in the production of aluminum sulphate. The potassium salt should be dissolved in the least possible quantity of boiling water. If a precipitate should form in mixing, apply heat to effect complete solution. When the liquid is cooled or evaporated, it affords transparent and regular

¹ In the organic compound, $\text{Al}(\text{CH}_3)_3$, and its homologues, however, the atom of Al is distinctly *triad*.

octahedral crystals,¹ which resemble fig. 135. They contain $\text{Al}^{\text{IV}}_2(\text{SO}_4)''_3$, $\text{K}'_2\text{SO}''_4$, $24\text{H}_2\text{O}$. This body is named *potash alum*, or simply *alum*. The solution of this salt has a sweetish but astringent taste, and acid reaction. The crystals effloresce superficially; they require thirteen times their weight of water for solution at 12.5°C ., and rather less than their own weight of boiling water. When the dry salt is heated gently it melts in its water of crystallisation, and is completely liquid at 94°C . When more strongly heated the water is driven off, and anhydrous alum ultimately obtained; during this process the mass froths up and a voluminous residue is obtained. If we exclude the water of crystallisation in ordinary alum, and, for the sake of brevity, write the sulphuric radicle as SO''_4 instead of $-\text{O}-\text{SO}''_2-\text{O}-$, we can represent the constitution of the alum thus:—

FIG. 135.



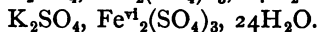
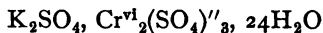
In our experiment we can substitute ammonium sulphate, $(\text{NH}'_4)_2\text{SO}_4$, for the potassium sulphate used, and thus get an *ammonium alum*, which crystallises in the same form as potash alum, and resembles the latter very closely in other particulars, save that it is

¹ If, prior to crystallisation, enough sodium carbonate be added to the solution to cause a distinct precipitate, and the latter be filtered off, the liquid affords cubic instead of octahedral crystals.

somewhat more soluble in water. This is the body often met with under the name 'alum.' It is the *Alumen*, B.P., and from it is prepared the *Alumen Exsiccatum*, B.P., or anhydrous alum, in the same way as the potash compound. On the large scale alum is manufactured from burnt shale or from 'alum clay'; either material is acted upon by sulphuric acid, and the resulting aluminum sulphate is mixed with the requisite quantity of crude ammonium sulphate, obtained from gas liquor, or crude potassium sulphate, and the resulting alum purified by crystallisation. A sodium alum is also known, but it is much more soluble in water than either of the two bodies already named. Several other metallic sulphates unite with aluminum sulphate and form bodies which more or less distinctly belong to the alum type, in containing 24 molecules of water by crystallisation, and in crystallising in octahedra or cubes modified by faces of the octahedron. For the present, however, we content ourselves with the recognition of the three alums.

Potash	.	.	$K'_2SO_4, Al^{vi}_2(SO_4)_3, 24H_2O.$
Soda	.	.	$Na'_2SO_4, Al^{vi}_2(SO_4)_3, 24H_2O.$
Ammonia	.	.	$(NH_4)'_2SO_4, Al^{vi}_2(SO_4)_3, 24H_2O.$

Now, since sodium or ammonium may replace potassium in alum without change of type, the question suggests itself whether other hexad groups can replace the Al^{vi}_2 in such compounds. Experiment 523 really supplied the answer, for we then obtained the body termed *chrome alum*, which is compared below with a similar compound which results from the union of *ferric* and potassium sulphates :—



Both these bodies are obtainable in octahedra, and therefore strictly conform to the type of alum, though they do not contain aluminum.

Experiment 582.—To a solution of common alum add ammonium hydrate, note that a gelatinous and translucent precipitate separates which is very slightly soluble in excess of the reagent. This body is so nearly transparent when separated from dilute liquids that its presence may be easily overlooked, but it becomes more dense on boiling, and is then more easily seen. This precipitate contains aluminum hydrate, $\text{Al}^{\text{vi}}_2(\text{OH})_6$.¹ When this compound is collected, dried, and heated to the temperature of boiling oil, the hydrate $\text{Al}_2\text{O}_2(\text{OH})_2$ is obtained. The latter is identical in composition with the native hydrate *diaspore*, while the former is represented by the mineral *gibbsite*. When either hydrate is heated to full redness all water is driven off, and the oxide Al_2O_3 is left ; the body is termed *alumina*. Aluminum hydrate produced from the sulphate, obtained as in Experiment 580, or from an alum, is the most convenient source of the salts of the metal ; thus by solution of the well-washed hydrate in hydrochloric acid a solution of the chloride $\text{Al}^{\text{vi}}_2\text{Cl}_6$ is obtained ;² if

¹ A soluble colloid hydrate is obtainable on dialysis by a precisely similar method to that employed in the preparation of dialysed iron ; see Experiment 551.

² The solution affords crystals of $\text{Al}_2\text{Cl}_6, 12\text{H}_2\text{O}$, but the anhydrous chloride cannot be obtained from them on heating.

hydrofluoric acid be used, we get the soluble fluoride, Al_2F_6 , a native compound of which is met with as the mineral *cryolite* (or ice stone, so named in allusion to its easy fusibility), whose formula is $\text{Al}_2\text{F}_6, 6\text{NaF}$; while if nitric acid is the solvent, the nitrate is formed and can be obtained in crystals consisting of $\text{Al}^{\text{VI}}_2(\text{NO}_3)_6, 16\text{H}_2\text{O}$: and so on for other salts. Any of these soluble compounds can again afford the hydrate on treatment with ammonium hydrate.

Gelatinous hydrate of aluminum possesses the remarkable property of abstracting many colouring matters from solution.

Experiment 583.—Bruise a few cochineal grains and boil them with water until much of the red colouring matter is extracted; then filter the liquid. To a portion of the coloured solution add some recently precipitated aluminum hydrate, and shake the mixture up. After standing for some time, filter the mixture, and note that the liquid which passes through the filter is nearly or quite decolourised, while the precipitate on the filter is a fine rosy colour. The latter when dried constitutes what is termed a *lake* by painters, and in a similar way various coloured lakes are produced for use as pigments. In most cases, however, the coloured liquid is first mixed with solution of alum, then on cautious addition of an alkali aluminum hydrate is precipitated, and carries down with it the colouring matter.

as decomposition occurs, alumina and hydrochloric acid resulting. The anhydrous chloride is best produced by the method described at p. 232, in connection with the separation of *aluminum*.

This experiment also proves that aluminum hydrate is a valuable *mordant* (see p. 55), and, in fact, it is largely used for this purpose, the tissue to be dyed being immersed in the first instance in a solution of any soluble aluminum salt and then in an alkaline carbonate solution, whereby the hydrate is separated in the tissue. The latter, when plunged into a bath of colouring matter, is then evenly dyed of the requisite tint. It is also employed in 'padding'—*i.e.* a pattern is printed in alum paste and the colour is extracted from the dye bath by the printed portion of the material.

Experiment 584.—Dry and ignite some of the aluminum hydrate in order to obtain alumina. Note that after ignition the oxide dissolves with much difficulty in acids, and the best mode of getting it again into a soluble condition is to fuse it with acid potassium sulphate, KHSO_4 ; the product then dissolves in water.

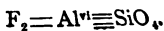
Experiment 585.—Support a fragment of alumina on a piece of charcoal or on a slip of platinum foil, and moisten it with a drop of cobalt nitrate or chloride solution, then heat for a short time in the Bunsen or blowpipe flame. Note that a beautiful *blue* colour is developed. This blue body is termed *cobalt ultramarine* or *Thenard's blue*, and its production serves as an excellent test for alumina. This blue is prepared on a large scale for use as a pigment.

Alumina when heated in the oxyhydrogen flame fuses, and crystallises on cooling. The minute crystals so obtained are identical with those of the mineral *corundum*. The latter is pure native alumina crystal-

lised in hexagonal forms ; it is colourless or bluish, and is of higher specific gravity than diamond, being nearly 4, while its hardness is but little less than that of diamond. It is met with in a crude and impure condition as *emery*, and when transparent and coloured by various metallic oxides it forms the gems *Oriental sapphire* (blue), *amethyst* (violet), *emerald* (green), *ruby* (red), and *Oriental topaz* (yellow).¹

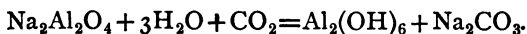
Experiment 586.—Instead of precipitating a solution of alum by ammonium hydrate add sodium or potassium hydrate, and note that the precipitate first formed dissolves in excess of the reagent, and the solution is found to contain the compound $\text{Na}_2\text{Al}_2\text{O}_4$ when sodium hydrate has been the solvent, or $\text{K}_2\text{Al}_2\text{O}_4$ with potassium hydrate. In these bodies the Al^{vi} plays an acidic part, though a feeble one. Compounds analogous to potassium aluminate are met with in nature, and constitute the group of *spinels*. The typical member of this group is the magnesium compound $\text{Mg}''\text{Al}_2\text{O}_4$, which is met with variously coloured, like corundum, as purple, red, yellowish or bluish *octahedral* crystals (Balas ruby, ruby spinel, rubicelle, and almandine). When a portion of the magnesium is replaced by Fe'' , a dark green mineral results named *pleonaste* ; and when iron almost wholly replaces Mg'' , black *picotite* is the product. Again, zinc can take the place of Mg'' , and afford *automolite*, or zinc spinel, $\text{Zn}''\text{Al}_2\text{O}_4$, without loss of octahedral form. Further, magnetic oxide

¹ The topaz of mineralogists is a silicofluoride of aluminum, whose formula is



of iron, $\text{Fe}''\text{Fe}_2\text{O}_4$, is octahedral and may be regarded as an iron spinel, as it conforms to the crystalline and chemical type of this group of minerals, and *chrome iron ore* (see p. 168) must be added to the list, as it also occurs in octahedral crystals, and conforms to the chemical type of the spinels.

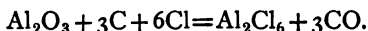
The ease with which caustic soda attacks alumina enables the latter to be conveniently prepared in a pure condition from *bauxite*. When the latter is fused with caustic soda soluble sodium aluminate is formed, and the iron always present (see p. 222) is left behind. When the solution of aluminate is treated with a current of carbon dioxide gas, sodium carbonate is formed and an aluminum hydrate is precipitated :—



The hydrate thus obtained is washed, dried, and ignited in order to afford pure alumina for use in the manufacture of metallic aluminum, and this treatment of bauxite is, in fact, the first stage in that manufacture. But alumina cannot be directly reduced to metal under any manageable conditions; the chloride of aluminum, however, is easily reduced by means of sodium. Hence conversion of alumina into anhydrous chloride must precede reduction, and the process we shall now carry out on the small scale exactly represents the larger operation.

Experiment 587.—Mix some anhydrous alumina with about half its weight of finely-powdered charcoal. When these materials are ground well together make the mixture into a stiff paste with oil, transfer the

mass to an earthenware crucible, cover the latter, and heat, gently at first, and then more strongly, until vapours cease to appear. The oil is thus decomposed and an intimate mixture of very finely divided carbon (chiefly derived from the decomposition of the oil) and alumina is obtained. Now break the black mass into small fragments and place them at one end of a rather wide tube of hard glass and heat strongly, while a current of well-dried chlorine gas is passed through the tube. After a time a whitish sublimate appears at the cooler part of the tube : this is the chloride sought, whose formula is $Al^{VI}_2Cl'_6$:—¹

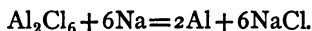


The chloride is a very deliquescent body and decomposed by water. It is volatile above $200^\circ C$. If the chloride be heated with half its weight of perfectly dry sodium chloride, the two bodies combine and form a double chloride, $Al_2Cl_6, 2NaCl$, which is liquid at $200^\circ C$., and when solidified on cooling does not decompose so rapidly in moist air ; hence it proves more manageable in the aluminum manufacture than the simple chloride.

The metal is reduced from the double chloride by heating the latter with about one-third of its weight of metallic sodium. When the reaction is over and the mass fused, some cryolite being added to facilitate

¹ The specific gravity of the vapour of this chloride is 134 ($H = 1$), hence the molecular weight is 268, which is almost identical with the theoretic number for Al_2Cl_6 . The formula of the body therefore should not be written $AlCl_3$.

liquefaction, the metal is obtained in molten masses. The essential reaction is :—



The metal though rather hard is malleable, white in appearance, and capable of fine polish. Its specific gravity is 2.55. The metal is so light and yet strong that it is now often used for the manufacture of optical and other instruments. When pure it resists tarnish well and is not attacked by sulphuretted hydrogen. It easily dissolves in most acids, and in caustic soda or potash with evolution of hydrogen.

Aluminum alloys with copper and then forms aluminum bronze, or 'Abyssinian gold,' which is largely employed in the production of cheap jewellery and other ornamental articles.

Experiment 588.—Add to a solution of alum some sulphuretted hydrogen water, and note that the reagent fails to cause a precipitate.

If to the same liquid ammonium sulphhydrate be added, a white precipitate appears ; but this is merely aluminum hydrate separated by the alkaline liquid, for a sulphide of aluminum cannot be formed in the wet way, though the metal directly combines with sulphur at a high temperature and forms the compound Al_2S_3 , the sulphur analogue of Al_2O_3 .

When pure alumina is heated with sulphur no change appears to take place ; but if an anhydrous aluminum silicate, such as ignited *kaolin*, $\text{Al}^{\text{VI}}_2\text{SiO}_7$ or $\text{O}=\text{Al}^{\text{VI}}_2(\text{SiO}_3)_2$, is heated with sulphur and sodium sulphate, a product is obtained which has a green colour, and the body when mixed with pure

sulphur and again heated becomes *blue*. This fine blue pigment is now manufactured in enormous quantities and is termed *ultramarine*.¹ Its precise nature is not known, but it is destroyed by acids with evolution of sulphuretted hydrogen gas; it is then inferred that it contains a sulphide, but whether of sodium or aluminum is uncertain.

A number of hydrated silicates of aluminum are known, some of which afford plastic masses when moistened with water, and then admit of moulding into various articles. When such articles are gradually dried and heated to redness the material does not fuse, but becomes hard and wear-resisting. Silicates capable of being thus worked are termed 'clays.' The purest form of clay is the fine white kaolin or porcelain clay, which is hydrated, and in its unburnt condition consists of $\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$. This body is a product of the decomposition of one or other of a group of native silicates termed 'felspars,' whose principal member is termed orthoclase and consists of $\text{K}_2\text{Al}_2\text{Si}_6\text{O}_{16}$. During the decomposition of the latter a potassium silicate is dissolved out, and kaolin is left along with more or less silica.

The finest kinds of *porcelain* are made from pure kaolin mixed with some fine white silica and a little unchanged felspar. When the moulded article is dry it is gently heated in order to effect dehydration, and then on cooling is painted with or dipped in a mixture of very finely divided felspar with water. The surface

¹ The beautiful blue mineral, *lapis lazuli*, is the native *ultramarine*.

is thus coated with the felspar, which is much more fusible than the clay. When the article is dry it is strongly heated up to the point at which fusion of the layer of felspar occurs, which thus coats the clay with a glossy film. The article when cold is white, sub-translucent, and coated with a varnish-like *glaze*, which renders it non-absorbent.

Common articles of *earthenware* are made from clay containing more or less iron and other impurities, which communicate a grey or red colour to the dish, jug, or tube, when finished. These articles are also glazed, in order to do away with the naturally porous condition of the burned clay, and, in the cases of finer articles, felspar is used, as with porcelain; but for rough utensils 'salt glazing' is resorted to. This consists in throwing common salt into the furnace; the salt is volatilised, and its vapour attaches to the surface of the earthenware articles, superficial layers of a fusible felspar-like silicate being formed, which thus glaze the material. A similar result is obtained by coating the articles with a mixture of borax and lead oxide before firing.

Ordinary *bricks* used in building are manufactured in a similar way, from clays that are still more impure; but even for these the proportions of chalk,¹ iron, and alkali must not be too great, else the bricks will 'slag' or fuse on baking. *Fire bricks* are made from highly siliceous clay, or fine quartz sand,

¹ Clays suitable for this purpose should not effervesce much when moistened with hydrochloric acid, indicating the presence of but a small proportion of chalk or limestone.

which contains only enough aluminum silicate to bind its particles together.

Closely related to aluminum are the rare metals GALLIUM, Ga = 69.8, which is met with in very small quantities in some specimens of zinc blende from Bensberg ; and INDIUM, In = 113.5, which occurs in the zinc blende of Freiberg. Both these metals were discovered by the aid of spectrum analysis, the former by Lecoq de Boisbaudran, and the latter by Rich and Richter. Another group of very rare metals is known whose members agree in forming earthy oxides like alumina and its related bodies. The elements referred to are CERIUM, Ce = 140, LANTHANUM, La = 180, DIDYMIUM, Di = 138, ERBIUM, Er = 170, TERBIUM, Tr = 149, YTTRIUM, Y = 89, and SCANDIUM, Sc = 44. Most of these are found in the rare minerals *Gadolinite* and *Cerite*.

CHAPTER XLI.

EXPERIMENTS WITH ZINC AND CADMIUM COMPOUNDS.

A REDDISH-BROWN mineral is often met with which may easily be mistaken for a poor ore of iron, or an ochre, but in reality is an amorphous mixture of ferric oxide with some clay and a carbonate of *zinc*. This ore is named *calamine* and is an important source of the metal zinc, which is manufactured in large quantities from it for industrial purposes. Zinc occurs in many other minerals, but notably as a sulphide in *blende*, or 'black-jack' of the miners, which is also worked for the metal. In most zinc ores small quantities of another metal, *cadmium*, are also met with and are separated in the manufacture of zinc. The two metals are thus very intimately associated in nature, and their extraction from the ores may be conveniently considered at the same time when we have made some experiments with the metals which are easily purchased in a sufficiently pure condition.

ZINC, $Zn''=65$.—This metal is of a bluish white colour, it can take a good polish and is not much affected by air and moisture. The specific gravity is about 7.1 (water=1), but varies within narrow

limits according to the way in which the metal has been worked. Commercial zinc usually contains small quantities of lead, iron and arsenic,¹ but these do not interfere with the use of the metal for ordinary chemical or other purposes. Sixty-nine parts of the metal contain at 100° C. the same quantity of heat as 108 parts of silver at the same temperature.

Experiment 589.—Place some scrap zinc in an iron ladle and heat ; the metal easily melts, its fusing point being 430° C. When molten pour some of the liquid metal from a height into water ; it solidifies in irregular masses and grains, and is then termed ‘granulated zinc’—*zincum granulatum*, B.P. Heat the residue in the ladle strongly, and note that vapour is given off which burns with a beautiful bluish-green flame, and quantities of white smoke are produced. The vapour² is that of zinc, which distils at 1040° C., and the smoke is oxide of zinc, ZnO, which is the product of the combustion of the vapour in air. Any of the oxide that is carried up falls after a time in wool-like flocks—the *lana philosophica* of the older chemists. Note that the oxide which attaches to the sides of the ladle is *yellow when hot*, though it becomes nearly white on cooling. Allow the contents of the ladle to cool down until any metallic zinc

¹ This impurity renders a sample of zinc useless for employment in Marsh’s test for arsenic, but the metal is easily purified by fusion with about one-fifth of its weight of nitre and frequent stirring. The arsenic is thus oxidised and separated as alkaline *arsenate*, and the pure metal left.

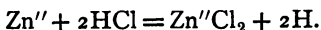
² The specific gravity of zinc vapour is 33 ($H = 1$), therefore the molecule of zinc gas contains only one atom.

remaining in it is near to the point of solidification, then pour the liquid metal out into an iron mortar previously warmed ; the metal solidifies, and if now beaten with the pestle it can be easily reduced to a fine powder, but only while its temperature is not less than $200^{\circ}\text{C}.$; between 150 and $130^{\circ}\text{C}.$ it is so malleable that it can be rolled out into sheets, while below $130^{\circ}\text{C}.$ it is again brittle.

When perfectly clean iron is plunged into molten zinc a layer of the latter becomes firmly attached to the iron, which is then said to be *galvanised*, and is enabled to resist atmospheric action.

We have already given the composition of the chief alloys of zinc—viz., brass (see p. 111), and nickel silver.

Experiment 590.—Add some strong hydrochloric acid to some granulated zinc contained in an evaporating dish. Hydrogen gas is evolved and the metal dissolves as chloride, thus :—



Continue the addition of acid until all the zinc disappears, and only a few dark flocks consisting of lead and carbon remain. Then boil the liquid for some time, and after dilution with some water filter the liquid. The latter is a powerful antiseptic and deodorising solution, and is often sold in a crude condition as *Burnett's disinfecting fluid*.

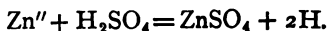
The solution we have obtained contains some iron in the condition of ferrous chloride, and, following the direction of the 'British Pharmacopœia,' the impurity

is removed by first converting the iron into ferric chloride by the addition of chlorine water, when



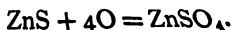
And then on shaking the cold liquid up with zinc carbonate ferric hydrate is precipitated and filtered off, zinc chloride is formed and some carbon dioxide gas is evolved. The colourless liquid thus obtained is evaporated down until an oily liquid is obtained, which solidifies on cooling to a white deliquescent mass, which is zinc chloride, ZnCl_2 , the *Zinci Chloridum*, B.P. This body is used in surgery as a caustic. Its solution acts as a powerful corrosive poison.

Experiment 591.—Make a similar experiment, adding diluted sulphuric acid to the zinc, which dissolves with the production of zinc sulphate :—



The solution is freed from iron in the same way as that of the chloride, and the liquid is then evaporated to the crystallising point when fine prisms are obtained, which consist of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. Six-sevenths of this water is expelled at 100°C . The crystals are soluble in about twice their weight of water. The salt is used as an emetic in medicine, and as an astringent and a tonic in cases of chorea.

Much of the zinc sulphate, or white vitriol of commerce, is obtained by roasting *blende*, ZnS , extracting the zinc sulphate from the residue by water and crystallising :—



Experiment 592.—To a solution of zinc sulphate add sodium carbonate, Na_2CO_3 , also in solution. Note that a white precipitate is formed and that gas is evolved with effervescence, which can be easily identified as carbon dioxide. Take care to add excess of the precipitant, *i.e.*, until the solution is slightly alkaline, then let the precipitate subside, after which decant the clear liquid and stir the precipitate with boiling water. Again decant the liquid and continue the washing until the wash water ceases to give a precipitate of barium sulphate on the addition of barium nitrate, followed by a few drops of hydrochloric acid. Collect and dry the precipitate, which is a basic zinc carbonate of variable composition, the *zinci carbonas*, B.P. This body approaches to the formula $\text{ZnCO}_3, 3\text{Zn}(\text{OH})'_2$. The normal carbonate ZnCO_3 is met with in nature in fine rhombohedral crystals, as *smithsonite* or pure *calamine*. Another zinc mineral is called *calamine*; this is the silicate $\text{Zn}_2\text{SiO}_4, \text{H}_2\text{O}$, but it is usually distinguished as *electric calamine*, as it is electrically excited by heat.

Zinc acetate, nitrate, and other soluble salts of the metal are easily formed by dissolving the precipitated basic carbonate in the respective acids.

Experiment 593.—Heat some zinc carbonate to redness in a crucible until a portion removed and tested with any acid no longer effervesces. The residue is zinc oxide, ZnO , water and carbon dioxide being expelled by heat.

This is a white, tasteless and inodorous powder, which becomes *yellow* on heating.

When almost any zinc compound is strongly heated.

on charcoal it is easily recognised, as an incrustation is obtained which is yellow when hot and white when cold. If the oxide be moistened with a drop of cobalt nitrate and again heated, a *green* colour is developed. This is prepared on the large scale for use as a pigment under the name of *Rinemann's green*.

Zinc oxide is largely used for white paint instead of white lead, as it is not discoloured by sulphuretted hydrogen. The oxide manufactured for this purpose is obtained by strongly heating a mixture of small coal and roasted calamine; the crude zinc oxide is thus reduced and the metal distils, but its vapour is allowed to come in contact with the air and it then burns, producing flocks of the oxide, which are carried along in a current of gas and allowed to deposit in successive chambers, whence the oxide is removed from time to time.

The *extraction of metallic zinc* from calamine is very simple in principle. The crude carbonate is roasted in order to drive off water and carbon dioxide, and the residue is mixed with coal as in the preparation of the oxide. The mixture is then strongly heated in retorts when reduction occurs, and the vapours of zinc evolved are condensed out of contact with the air. The first portions that come over contain the *cadmium* present in the ore, as that metal is converted into vapour at 860° C., and is therefore more volatile than zinc (from which it is purified by a second distillation). The zinc is then condensed, fused, and cast into ingots.

Experiment 594.—To a solution of zinc sulphate add sodium hydrate, note that a white precipitate of zinc hydrate, $\text{Zn}(\text{OH})_2$, forms, which is easily soluble in

excess, like aluminum hydrate, and the compound $(\text{NaO})_2\text{Zn}$ is formed. The same body is produced with evolution of hydrogen by dissolving metallic zinc in sodium hydrate at the boiling temperature.

Experiment 595.—Make a similar experiment with ammonium hydrate, and note that a white precipitate of hydrate is formed, which is also soluble in excess of the reagent.

Experiment 596.—Add a few drops of hydrochloric acid to a solution of zinc sulphate, and then some sulphuretted hydrogen water. No change follows the treatment, but when ammonium hydrate and ammonium sulphhydrate are added, a *white* precipitate of hydrated zinc sulphide, ZnS , separates, which is soluble in hydrochloric, nitric, and sulphuric acids, but is *not* dissolved by acetic acid, and can therefore be precipitated from a zinc solution containing that acid. This is the only white sulphide known.

The native sulphide, *blende*, has the same composition as that precipitate, and its colour varies from pale brownish to black ; in the latter specimens iron is usually present.

Throughout our experiments with zinc, no traces of any compounds have been obtained in which the metal acts with any higher atomicity than that of a diad, as in the chloride $\text{Zn}''\text{Cl}_2$. Nor are any compounds known in which the element acts as an apparent monad, like mercury in mercurous compounds ; nevertheless, its crystallised sulphate resembles that of iron (ferrous sulphate) in composition, and it shares with lead (and magnesium) on one side and aluminum on the other a tendency to form basic salts.

CADMIUM, $\text{Cd}''=112$.—The mode of separating this metal from zinc has been already stated. Cadmium is whiter than zinc, and is less brittle at ordinary temperature. Its specific gravity is 8.45, and it melts at 315°C . Cadmium distils at 860°C ., and the specific gravity of its vapour is 55.8 ($\text{H}=1$), therefore the molecule of cadmium gas, like that of zinc, contains but one atom. The weight of cadmium that contains, at 100°C ., the same quantity of heat as 108 parts of silver at the same temperature is 116 parts.

There are very few compounds of the metal in general use, and we shall deal only with them in the following experiments.

Experiment 597.—Heat some fragments of metallic cadmium with twice their weight of iodine and enough water to cover the mixture. Solution takes place as in the case of ferrous iodide (Experiment 536), and the colour of the iodide disappears; after a time a colourless solution is obtained, as the cadmium used is in excess of the iodine, and the liquid, when filtered and evaporated, affords beautiful pearly crystalline plates of cadmium iodide, whose composition is represented by the formula CdI_2 . A corresponding chloride is easily obtained by solution of the metal in hydrochloric acid, and a nitrate or sulphate by solution in the suitable acid.

Experiment 598.—Add to the solution of any soluble salt of cadmium some sodium hydrate; note that a white precipitate is obtained of cadmium hydrate, $\text{Cd}(\text{OH})_2$, which is not soluble in excess of the reagent.

When this white precipitate is washed, dried, and

heated strongly, a *brown* residue of cadmium oxide, CdO , is obtained. Any cadmium compound when heated on charcoal in the blowpipe flame affords a very characteristic brown incrustation of this oxide.

Experiment 599.—Add ammonium hydrate to a cadmium solution, and note that a white precipitate is obtained as in the last case, but it easily dissolves in excess of the reagent, and affords a colourless liquid.

Experiment 600.—Add to a solution of cadmium iodide a drop or two of hydrochloric acid ; no precipitate appears, but on the addition of sulphuretted hydrogen in excess, a bright yellow sulphide, CdS , separates.¹ This sulphide, unlike the sulphides of mercury, copper, bismuth, and lead, is soluble in boiling dilute sulphuric acid. Cadmium sulphide is not dissolved by ammonium hydrate or ammonium sulphhydrate, and is remarkable as the *only yellow sulphide* not dissolved by the last named reagent.

Sulphide of cadmium prepared as above is used as a fine yellow pigment ; it possesses the great advantage of being wholly unaffected by sulphuretted hydrogen gas.

The mineral *greenockite* is the native form of cadmium sulphide. Cadmium, like zinc, only forms one class of compounds in which the metal acts as a diad.

¹ The precipitation of this body is seriously interfered with by a great excess of hydrochloric acid.

CHAPTER XLII.

EXPERIMENTS WITH MAGNESIUM COMPOUNDS.

MAGNESIUM, $Mg''=24$.—It is often difficult to distinguish, by mere inspection, between specimens of zinc sulphate and the well-known 'Epsom Salt';¹ but the latter compound is the sulphate of the diad metal *magnesium*, and can be easily recognised by the chemical characters to be presently noted. Nevertheless, the resemblance between the compounds is by no means superficial, for not only are they isomorphous—crystallising in trimetric prisms—but the magnesium salt contains $MgSO_4, 7H_2O$, and thus agrees with the zinc sulphate in degree of hydration. Other compounds of the metals are similar in physical characters and in composition; hence the study of magnesium naturally succeeds that of zinc.

As 'Epsom salt' is the compound of the metal

¹ So called because it is the chief saline constituent of a mineral water met with at Epsom, in Surrey, a district noted for its races as well as springs. Epsom water contains about 30 grammes per litre of the salt. Several other mineral waters, notably those of Seidlitz, in Bohemia, and of Pullna, owe much of their efficacy as aperients to the presence of the same compound.

which is used as the source of most other magnesium salts, we shall examine it first.

Magnesium sulphate, with only one molecule of water, is met with in nature in large quantities, as the mineral *kieserite*, $\text{MgSO}_4, \text{H}_2\text{O}$. This compound, unlike Epsom salt, is very slowly soluble in cold water—hence the impurities that accompany it, and which are generally more soluble, are easily washed away; the purified *kieserite* is then treated with hot water, in which it dissolves, undergoing conversion into Epsom salt by combination with six molecules of water. Much of the Epsom salt of commerce is now obtained in this way, though some is prepared by the solution of the native carbonate, *magnesite*, MgCO_3 , or of dolomite (see p. 258) in diluted sulphuric acid. The crystals of Epsom salt are soluble in four times their weight of cold water, and the solution has a bitter taste, which is perfectly distinct from the metallic astringent taste of the zinc compound.

Experiment 601.—Heat some Epsom salt in a porcelain crucible; it fuses in its water of crystallisation first, and then dries up as it parts with water until, when the temperature has reached 180°C ., a white and slowly soluble monohydrated sulphate is obtained, whose composition is identical with the mineral *kieserite*.

Experiment 602.—Add sodium carbonate solution to one of Epsom salt, and note that a white precipitate of magnesium carbonate is obtained, while carbon dioxide gas is evolved, as in the corresponding case of zinc carbonate. When the mixture is boiled *with much water* it becomes less gelatinous than

when first precipitated, and can be easily washed on a filter with hot water, and dried at 100° C. As thus obtained, the carbonate is a light white powder, and is the *magnesiæ carbonas lævis*, B.P. A much more dense powder is obtained if the precipitation is effected in strong solutions, the mixture *evaporated to dryness*, and the soluble sodium sulphate washed out with boiling water. The residue is the *magnesiæ carbonas*, B.P., or the 'heavy' carbonate.

Obtained in either way, the carbonate is hydrated, basic, and somewhat variable in composition; like the corresponding zinc compound, the formula given in the 'British Pharmacopœia,' $(\text{MgCO}_3)_3, \text{MgO}, 5\text{H}_2\text{O}$, can only be regarded as an approximate expression for the body.

Magnesium carbonate, especially the 'light' variety, though very slightly soluble in pure water, is dissolved with comparative ease by carbonic acid water, especially under pressure. *Sir James Murray's* and *Dinneford's fluid magnesia*, now much used in medicine, is such a solution of the carbonate. This solution when allowed to lose carbon dioxide gas slowly deposits crystals of the hydrated normal carbonate, $\text{MgCO}_3, 3\text{H}_2\text{O}$. This carbonate occurs native, but anhydrous, as the mineral *magnesite*, and in union with calcium carbonate as *dolomite* (see p. 258).

Experiment 603.—Ignite in a crucible either of the precipitated carbonates obtained as above, and continue heating until a portion dropped into dilute sulphuric acid no longer effervesces. When the 'light' carbonate is used the *magnesia levis*, B.P., is obtained, which is a bulky white powder nearly

3.5 times the bulk of an equal weight of the 'calcined magnesia' similarly obtained by the ignition of the 'heavy' carbonate.

There is no chemical difference between the products, as the residue in each case consists of magnesium oxide, MgO , and is identical with the body produced when metallic magnesium was burned in air in Experiment 2. The oxide is very slightly soluble in water: it is met with as the mineral *periclase*.

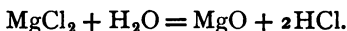
Experiment 604.—Add ammonium hydrate to solution of magnesium sulphate, and note that a white precipitate is formed, which is magnesium hydrate $\text{Mg}''(\text{OH})'_2$. Now pour in some solution of ammonium chloride, NH_4Cl , and shake, when the hydrate disappears and a clear liquid is obtained. Generally, magnesium hydrate is not precipitated by ammonium hydrate from solutions containing much ammonium salts, nor does ammonium sulphhydrate precipitate such solutions, as a sulphide of magnesium has not been obtained from solution. Potassium, sodium, and barium hydrates precipitate $\text{Mg}(\text{OH})_2$. The foliated mineral *brucite* is the native form of magnesium hydrate.

Experiment 605.—If to the solution of magnesium hydrate in excess of ammonium hydrate and chloride obtained in the last experiment we add sodium hydrogen phosphate, a precipitate forms which consists of $\text{Mg}''\text{NH}'_4\text{PO}_4, 6\text{H}_2\text{O}$. This result is identical with that obtained in Experiment 345 (see Part II. for the characters of the precipitate).

The following well-known minerals are magnesium *silicates*—

Talc (steatite, soapstone)	.	(Mg''H' ₂)SiO ₃ .
Meerschaum	.	(Mg''H' ₂)SiO ₃ + H ₂ O.
Serpentine	.	(Mg''H' ₂) ₂ SiO ₄ .
Asbestos	.	(Mg''Ca'')SiO ₃ .

Experiment 606.—Add magnesium carbonate to hydrochloric acid as long as solution takes place. When the liquid is evaporated to a small bulk crystals separate, which consist of $\text{MgCl}_2, 6\text{H}_2\text{O}$. If the solution be evaporated to complete dryness a residue of magnesia is obtained, as magnesium chloride, like that of aluminum, suffers decomposition during the expulsion of the last portion of water, thus :—

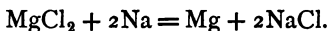


The anhydrous chloride, therefore, cannot be obtained from the simple solution of the salt. Nor can it be prepared by the method followed in the case of aluminum chloride. If, however, the aqueous solution of magnesium chloride, prepared as above, be mixed with ammonium chloride, a double chloride is formed,¹ the solution of which may be evaporated to dryness without decomposition, and the residue when strongly heated parts with the ammonium chloride, while the anhydrous magnesium chloride remains.

Metallic magnesium is obtained by heating in a crucible a mixture of the anhydrous chloride with half its weight of metallic sodium, some fluor spar being added as a flux. Energetic action takes place, and

¹ The mineral *carnallite* is a potassium double chloride, containing $\text{MgCl}_2, \text{KCl}, 6\text{H}_2\text{O}$. This is now much used as a source of magnesium and potassium salts.

magnesium is obtained as a molten layer at the bottom of the crucible.



The metal can be purified by distillation as it is volatile at a red heat. It is silvery white and does not tarnish in pure dry air. When in a semi-fluid state it can be drawn into wire, and the latter when rolled is converted into magnesium ribbon, which is employed for pyrotechnic purposes, as it emits a brilliant light when burning in air or oxygen, and this light being rich in chemically active rays is employed for photographic purposes, and for bringing about chemical changes of other kinds.

The rare element, *Beryllium* or *Glucinum* (so named in allusion to the sweet taste of solutions of its salts), Be'' or $G''=9.2$, is chiefly met with in *beryl*—a silicate of beryllium and aluminum. It is naturally related on one side to zinc and magnesium, and on the other to the group of metals to be dealt with in the next chapter.

CHAPTER XLIII.

EXPERIMENTS WITH CALCIUM, STRONTIUM, AND
BARIUM COMPOUNDS.

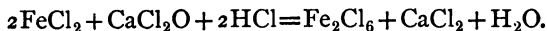
A SMALL group of diad metals occupy a distinct position between zinc and magnesium and the monad alkaline metals, potassium and sodium. This group contains three members, namely, CALCIUM, STRONTIUM and BARIUM;¹ of these the first is the most important, as the base of well-known lime compounds. The metals themselves have not been applied to any useful purposes, and they have been obtained with difficulty by the electrolysis of the corresponding chlorides when the latter were in a fused condition. *Calcium* is a soft, yellowish metal, of specific gravity 1.57; *strontium* is also yellow, but of specific gravity 2.5; while *barium* is silvery white, and its specific gravity is at least 4.0. All these are so easily oxidised on exposure to the air that they are kept under naphtha or other liquid free from oxygen.

CALCIUM, $\text{Ca}''=40$.—There are few minerals more commonly met with than the carbonate of the metal

¹ Often termed metals of the 'alkaline earths,' as their oxides and hydrates are somewhat earthy in general characters, while strongly alkaline in reaction.

calcium—the source of most compounds of the element. It constitutes the amorphous or sub-crystalline *chalk* of which the ‘white cliffs of Albion’ (*i.e.*, Dover) are formed, the variously coloured and crystalline *marble* as well as common *limestone* ; while in its purest condition it appears as the beautiful transparent *calc spar* or *Iceland spar*, which occurs in rhombohedra, or of *arragonite*, which is the same compound in trimetric prisms. As white marble is the purest form of calcium carbonate which is easily obtained we shall commence our experiments with that body, and use it as a source of the chief calcium compounds.

Experiment 607.—Add marble, broken in small pieces, to hydrochloric acid until effervescence (consequent on the escape of carbon dioxide gas) no longer occurs on addition of fresh fragments ; or take at once the solution contained in the bottle used in Experiment 231 in the generation of carbon dioxide gas. The solution usually contains a little iron, which can be easily removed by adding a few drops of solution of bleaching lime, when ferrous chloride passes into ferric chloride, thus :—



On then boiling the liquid with some finely powdered marble the iron is separated as hydrate, and can be filtered off. The solution, when evaporated to a syrupy consistence, slowly forms very deliquescent crystals, which contain $\text{CaCl}_2, 6\text{H}_2\text{O}$. If the solution be rapidly evaporated to dryness, and the solid residue heated to 200°C ., the hydrate $\text{CaCl}_2, 2\text{H}_2\text{O}$ is left. A

dry porous mass is thus obtained which is admirably suited for drying gases, as it absorbs moisture with great avidity and it exposes a very large drying surface. When heated to redness all water is driven off, and CaCl_2 is obtained in a fused condition; this solidifies on cooling to a white mass, which is also used as a dehydrating agent, but is not as effective in practice as the porous hydrate. As already stated, the metal is obtained from the anhydrous chloride by electrolysis.

The so-called 'chloride of lime' is not to be confounded with the above compound. The preparation and composition of that important bleaching material have been considered under Experiment 152.

Experiment 608.—Introduce a platinum wire charged with a drop of calcium chloride solution into the Bunsen flame. Note that an *orange-red* colour is developed. Most compounds of calcium when moistened with hydrochloric acid afford this flame reaction.

Experiment 609.—Add to solution of calcium chloride a solution of potassium fluoride, obtained by neutralising caustic potash with hydrofluoric acid, and note that a white precipitate forms; this is calcium fluoride, CaF_2 . This precipitate is identical in composition with the mineral 'fluor spar'¹ (see Experiment 200, *et seq.*), or Derbyshire spar, which is found crystallised in variously coloured and more or less modified cubes.

¹ So named because when used as a flux in smelting metallic ores it increases the fluidity of a molten mass, *i.e.*, makes it flow easily.

Experiment 610.—Dissolve some chalk or marble in nitric acid; a solution of calcium nitrate, $\text{Ca}(\text{NO}_3)_2$, is thus easily obtained. This salt does not possess any special interest.

Experiment 611.—Add chalk or marble to diluted sulphuric acid, and note that, while gas is evolved at first, the evolution soon ceases, and the particles of marble or chalk are seen to be coated with a white body. If, however, the mixture be agitated,¹ so as to detach the coating, gas is again evolved as fresh surfaces of chalk are presented for attack by the acid. The white body must be calcium sulphate, and is obviously either nearly or quite insoluble. The reaction when completed is—



Owing to the evidently low solubility of calcium sulphate it should be possible to prepare it by precipitation. Hence we make

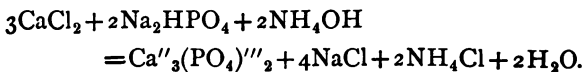
Experiment 612.—Add to calcium chloride solution any dissolved sulphate—ammonium sulphate for example; a precipitate of calcium sulphate quickly forms. If the solutions are very dilute a precipitate is not obtained, as the sulphate is sensibly though slightly soluble in water (one part in 450). It easily dissolves in excess of the ammonium sulphate on boiling, and in sodium thiosulphate solution.

Calcium sulphate is met with in nature as the

¹ In the 'soda water' manufacture carbon dioxide gas is obtained as above, and a mechanical stirrer is employed in the generating vessel in order to keep up the action and render it nearly complete.

minerals *anhydrite* and *gypsum* or *selenite*. The former is the compound CaSO_4 , the latter $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. When gypsum is heated to a temperature not exceeding 120°C . it parts with all its water, and yet the residue retains the power of recombining with water in order to form the original body. Gypsum thus dehydrated constitutes the well-known *plaster of Paris*, and the 'setting' of the latter to a solid mass when made into a thin paste with water is due to the rehydration of the calcium sulphate. If, however, the gypsum be heated in the first instance to 220°C . the residue passes into the *anhydrite* condition, in which it very slowly combines with water. Such 'over-burnt' plaster is practically useless.

Experiment 613.—Add to solution of calcium chloride some common 'phosphate of soda' solution, followed by sufficient ammonium hydrate to render the liquid alkaline. Note that a white, somewhat gelatinous, precipitate is formed; this is calcium phosphate, $\text{Ca}''_3(\text{PO}_4)'''_2$, in a hydrated condition:—

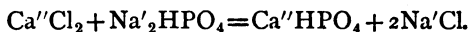


This phosphate¹ is easily dissolved by ammoniacal salts and by acids. This body is met with in nature in hexagonal crystals as *apatite*, a mineral which contains calcium fluoride, and a little chloride as well as phosphate. Its formula is $3[\text{Ca}''_3(\text{PO}_4)'''_2] + \text{Ca}''(\text{F}'\text{Cl}')_2$.

¹ The *calcis phosphas*, B.P., is obtained by first dissolving bone ash in hydrochloric acid, and then precipitating the calcium phosphate with excess of ammonium hydrate.

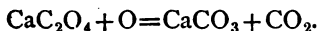
Calcium phosphate is the chief mineral constituent of bone, of coprolites, and of guano—the partially decomposed excrement of sea birds.

Experiment 614.—Repeat the last experiment, omitting the ammonium hydrate; a precipitate forms which is less gelatinous than that last produced. This contains Ca''HPO_4 .

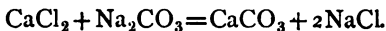


Two other phosphates, viz., $\text{H}_4\text{Ca''}(\text{PO}_4)'''_2$ and $\text{Ca''}(\text{PO}_3)'_2$, have already been noticed under Experiment 339.

Experiment 615.—Add ammonium oxalate, $\text{NH}_4)'_2\text{C}_2\text{O}_4$, to solution of calcium chloride; a white precipitate is formed which consists of calcium oxalate, $\text{Ca''C}_2\text{O}_4$. This precipitate if allowed to remain in the liquid for some time becomes distinctly crystalline, and appears under the microscope to be made up of small but beautiful octahedra. It occasionally occurs in urine, and forms the ‘mulberry calculus.’ The precipitate is insoluble in acetic acid, but is easily dissolved by hydrochloric or nitric acid. When the compound is dry and is then heated in the air it decomposes thus :—



Experiment 616.—Add sodium carbonate in excess to solution of calcium chloride, and note that a white precipitate is formed: this is calcium carbonate,



The precipitate when collected, washed well, and dried,

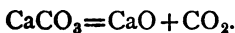
constitutes 'Precipitated Chalk,' or *calcis carbonas precipitata*, B.P. We have already learned from Experiment 239 that calcium carbonate is soluble in carbonic acid, and that from such a solution the *stalactitic* forms of the mineral are obtained ; the student is recommended to refer to that experiment, and to 240, repeating them if necessary.

We have indicated at the commencement of this chapter most of the various forms in which calcium carbonate is met with in nature, and shall not dwell upon them here, but we have not hitherto mentioned a *compound* of calcium and magnesium carbonates, which occurs in great masses as *magnesian limestone*, often mistaken for ordinary limestone, and is sometimes found in well-defined rhombohedral crystals, as the mineral *dolomite*, $\text{CaCO}_3 + \text{MgCO}_3$.

Experiment 617.—Digest dolomitic limestone with diluted sulphuric acid, calcium sulphate is then formed, and dissolves in the liquid to a very small extent; magnesium sulphate is also formed but is easily soluble, and can be crystallised from the filtered liquid, or the solution can be tested for magnesium by sodium hydrogen phosphate, after the addition of ammonium chloride and carbonate. Any precipitate caused by the latter reagent must be filtered off before adding the phosphate solution, else any calcium dissolved as sulphate may be mistaken for magnesium.

Ordinary limestone is used as a building material, though it is not well suited for towns in which much *acid vapour* and smoke impregnate the atmosphere ; *it is*, however, chiefly employed in the production of *lime* for mortar and cement.

Experiment 618.—Throw a few fragments of hard chalk, marble, or limestone into an ordinary bright fire ; after heating to redness for half an hour or so pick out one of the pieces ; while the mineral has not lost its form, it has altered much in its chemical characters, for, if it has been heated long enough, a fragment does not now effervesce briskly with hydrochloric acid, as it has lost carbon dioxide, and been converted into simple calcium oxide ¹ or *quicklime* :—



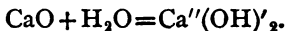
Limestone is burned on the large scale in deep brick pits, which are usually built against the face of some cutting, so that there may be easy access to the top and bottom of the kiln. A fire is started in the furnace, and then limestone and coal, or rough fuel of any kind, are thrown in from above until the kiln is full. Combustion proceeds throughout the mass, during the progress of which carbon dioxide is given off in abundance ; when the fuel has burned out the mass is allowed to cool down, and the lime is raked out at the base of the kiln.

Quicklime, as thus obtained from good limestone, is greyish white, and it is able to withstand the high temperature of the oxyhydrogen flame without fusion.

Experiment 619.—Pour some distilled water over a lump of fresh quicklime. The water is quickly absorbed, if too much be not added at one time,

¹ A dioxide, CaO_2 , also exists, and is obtained by precipitating lime water with hydrogen peroxide. At least two sulphides of calcium are known, CaS and the CaS_2 —the latter was formed in Experiment 287.

soon the temperature rises, steam is evolved, and the mass changes to a soft, white, and bulky powder.¹ The heat evolved, which is often sufficient to raise the temperature of the mass to 300° C., is due to the chemical action in progress, which results in the production of calcium hydrate, $\text{Ca}(\text{OH})_2$, or 'slaked lime':—



The hydrate when diffused through water forms 'milk of lime,' but the weight actually dissolved by the water is very small, since 1 litre of water at mean temperature dissolves only 1·25 gramme, while at the boiling point 0·75 gramme remains in solution, the excess being precipitated. The *aqua calcis*, B.P., or 'lime water,' is obtained by shaking up with water more calcium hydrate than the liquid can dissolve; the excess is allowed to deposit, and the clear liquid is then drawn off for use. This solution has a strongly alkaline reaction to test-paper and neutralises acid, hence the hydrate is powerfully basic. We already know, from Experiments 88, 231, 237, and 239, that it easily unites with carbon dioxide gas and reproduces chalk. Lime is much used in agriculture for the purpose of hastening the decomposition of organic constituents of the soil, and of breaking up the silicates containing potassium and sodium, in order that the latter may be set free to aid in plant nutrition. The principal use of slaked lime is in the preparation of the MORTAR used by brick-

¹ Lime obtained from dolomitic limestone does not slake well, and is technically termed 'poor.'

layers and stonemasons. This is a mixture of sand with about one-third of calcium hydrate. When placed between bricks it adheres to the surfaces, and ultimately binds them together; at first the mixture gradually dries, and absorption by carbon dioxide gas from the air proceeds slowly, calcium carbonate being formed, which leads to the hardening of the mass; this would occur in time even in the absence of sand, but the consolidation is hastened by the presence of the already solid particles which are cemented together by the carbonate. The complete conversion of the hydrate into carbonate is an extremely slow process.

Many limestones and calcareous deposits are met with which contain more or less clay, or aluminum silicate. When the proportion of the latter reaches 20 or 30 per cent., and the material, after grinding, is carefully burned so as to drive off carbon dioxide from the calcium carbonate, a powder is obtained which rapidly 'sets' even under water, and is therefore a water-resisting or 'hydraulic cement.' The well-known red 'Roman cement' is thus prepared from nodules of septaria, while artificial mixtures of clay and chalk are made which, when burned, afford similar products—'Portland cement,' for example—and the rate of hardening of the cement can be regulated by varying the proportion of clay, as slow setting is obtained with a smaller amount of clay. Engineers of large experience in the use of cements of this class generally prefer those which set at a moderate rate rather than with great rapidity, as the product is then *more durable*.

The theory of 'setting' of hydraulic cement is by no means established, as some believe that it is wholly due to absorption of carbon dioxide, as in the case of ordinary mortar ; while the older view was that in moistening the mass chemical action takes place between the constituents of the cement, resulting in the formation of more or less hydrated and insoluble silicates of aluminum and calcium, of which the hard mass was supposed to consist. That the first view is not wholly correct is proved by the fact that some cements set well even when carbon dioxide is excluded ; while the older theory does not adequately account for the firm adhesion of the cement to the stone to which it is applied.

STRONTIUM, $Sr''=87.2$.—The chief native compound of this element is the carbonate *strontianite*, named from Strontian in Scotland, the locality in which it was originally obtained. The composition of this carbonate is represented by the formula $SrCO_3$. When the mineral is dissolved in diluted nitric acid, carbon dioxide gas is evolved, and strontium nitrate, $Sr''(NO_3)_2$, is obtained in solution. The solid salt is easily separated on evaporation by the liquid ; similarly the chloride, $SrCl_2$, is prepared by dissolving strontianite in hydrochloric acid. The nitrate is the compound of the metal, which is most easily obtained, and with it most of the following experiments can be performed:—

Experiment 620.—Hold a crystal of the nitrate in the Bunsen gas flame on a platinum wire, and note the vivid red colour produced. This is a good test

for strontium, and the production of a bright red light has led to the extensive use of the nitrate in the preparation of fireworks and port-fires ; indeed strontium compounds are almost exclusively used for this purpose.

A good *red fire* is thus prepared. Powder 4 grammes of potassium chlorate, and mix with it 16 grammes of perfectly dry strontium nitrate also in powder, then add 5 grammes of sulphur, and one gramme of common lampblack. These materials must not be rubbed hard in a mortar, lest they take fire, but should be mixed on a sheet of paper. A small portion when touched with a match burns with a fine red light.

Experiment 621.—To solution of strontium nitrate add ammonium carbonate. A white precipitate of the carbonate, SrCO_3 , is produced. This body, when strongly heated, parts with most of its carbon dioxide, and a residue of the oxide, SrO , is obtained, but it is difficult to drive off all the carbon dioxide ; hence it is better to ignite the nitrate, which leaves pure strontium oxide. When water acts upon this body strontium hydrate, Sr(OH)_2 , is produced.

A dioxide analogous to calcium dioxide is also known.

Experiment 622.—Add to a solution of strontium nitrate a saturated solution of calcium sulphate in water. A white precipitate appears *after some time*. This is strontium sulphate, which is insoluble in water and acids. Its composition is SrSO_4 ; this body is met with in nature as the mineral *celestine*, which is often associated with specimens of native sulphur. *Strontium sulphate*, unlike that of calcium, is not dis-

solved by a boiling solution of ammonium sulphate. Calcium sulphate is used in the above experiment because its solution serves better than that of any other sulphate to distinguish Sr from Ba. (See Experiment 629.)

The other compounds of this element are not of sufficient general importance to require notice.

BARIUM, Ba''=137.—The carbonate of barium is a rather common mineral named *witherite*, whose formula is Ba''CO₃. This body is insoluble in water, but is easily soluble in acids.

Experiment 623.—Dissolve some witherite in diluted hydrochloric acid. Effervescence occurs, owing to the escape of carbon dioxide gas. The mineral is added until effervescence ceases, and a solution is obtained, which affords on evaporation crystals of the compound BaCl₂, 2H₂O:—



The salt is soluble in about three times its weight of pure water; but the compound is easily precipitated from this solution by either hydrochloric or nitric acid, as it is much less soluble in these acids than in water. This point must be borne in mind, else barium may easily be mistaken for certain other metals in the course of analysis; barium chloride thus separated is, however, easily redissolved by addition of water only.

Experiment 624.—Introduce on a platinum wire a little barium chloride into a Bunsen flame, and note that a *green* colour is communicated to the flame. This is a convenient test for the metal, as most of its com-

pounds when moistened with strong hydrochloric acid and heated give the flame reaction.

Experiment 625.—Add witherite in excess to diluted nitric acid. When all the acid has been neutralised, filter and evaporate the solution until crystals appear. On cooling, barium nitrate, $\text{Ba}(\text{NO}_3)_2$, separates in anhydrous crystals. This compound is much used in qualitative analysis for the detection of the acid radicles of Groups I. and II. by precipitation (see Analytical Appendix to Part II.), consequently the barium salts of those radicles are most easily prepared by the addition of the soluble neutral salts of the radicles to barium nitrate solution. The nitrate is used by pyrotechnists in the same way as strontium nitrate, but for the production of *green fire*.

Experiment 626.—Add to solution of barium nitrate some hydrofluosilicic acid, as in Experiment 209; a crystalline precipitate of barium silicofluoride, $\text{Ba}''\text{SiF}_6$, is formed, which is increased by addition of alcohol, and is not soluble in hydrochloric acid. Calcium and strontium salts do not afford a precipitate with the reagent. Another good distinctive test is the following:—

Experiment 627.—Add potassium chromate solution to *neutral* solution of barium nitrate; a *yellow* precipitate forms of $\text{Ba}''\text{CrO}_4$, which is easily soluble in hydrochloric or nitric acid.

Experiment 628.—Add ammonium carbonate to solution of barium nitrate; a white precipitate forms, which consists of BaCO_3 , in an amorphous condition, whereas the native compound witherite occurs in

trimetric prisms whose specific gravity is high—viz. 4.3 (water=1).

When the carbonate is strongly heated it parts with a portion only of its carbon dioxide, unless the temperature is very high. In this respect it is unlike calcium carbonate, and approaches more closely to the potassium and sodium carbonates, which do not part with any carbon dioxide, even at a bright red heat. Strontium carbonate loses carbon dioxide less readily than chalk, but much more easily than barium carbonate, and in this respect occupies an intermediate position between the remaining two members of this natural group. This position is quite in accordance with the atomic weight of strontium, which is the mean of the weights of calcium and barium; thus $(40 + 137) \div 2 = 88.5$, whereas the experimental number for strontium is 87.2.

Experiment 629.—Add a saturated solution of calcium sulphate to barium nitrate solution. A white precipitate is formed *immediately*, unless there happens to be much free acid present. The precipitate consists of $Ba''SO_4$, which is insoluble in water and almost unaffected by dilute acids, though sensibly soluble in concentrated hydrochloric acid.

If ammonium sulphate be used as the precipitant the barium sulphate is dissolved to a very small extent by excess of the reagent.

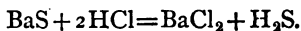
Barium sulphate is frequently met with as the mineral '*heavy spar*,' which occurs in trimetric prisms, and derives its name from its high specific gravity—4.5—as compared with other mineral sulphates. *Although this mineral is peculiarly difficult of direct*

solution, it is the chief source of soluble barium compounds,¹ which are, however, obtained from it indirectly, as under.

Experiment 630.—Mix with dry and very finely powdered barium sulphate about one-third of its weight of charcoal in fine powder, and mix into a paste with oil. Throw the mixture into a clay crucible, cover the latter loosely, heat to full redness, and then allow to cool. A portion of the residue in the crucible if treated with a few drops of hydrochloric acid evolves sulphuretted hydrogen gas, while barium chloride is obtained in solution. Hence the sulphate has been reduced to sulphide of barium² by the charcoal, thus:—



Then on addition of hydrochloric acid the sulphide is decomposed:—



The nitrate may be obtained by the action of *diluted* nitric acid on the sulphide; if the strong acid were used, it would oxidise the compound and reconvert it into sulphate.

As we have seen, barium carbonate, unlike chalk, does not part with much carbon dioxide at manageable temperatures, hence we take advantage of the easy decomposition of the nitrate in order to obtain the oxide of the metal.

¹ The finely ground mineral or precipitated sulphate is used as a substitute for white lead in paint, and is largely employed as an adulterant of the more expensive pigment.

² The sulphide can be dissolved by boiling water.

Experiment 631.—Throw into an iron ladle heated to redness small successive quantities of barium nitrate ; the salt fuses and gives off oxides of nitrogen with much troublesome effervescence ; but by allowing each charge of nitrate time to decompose, a whitish mass is obtained, which consists of the oxide BaO .

Experiment 632.—Add fragments of the oxide to cold water, note that heat is evolved as in ‘slaking’ lime, and the hydrate Ba(OH)_2 is first formed, which dissolves in about thirty parts of cold water and in less than twice its weight of boiling water. When the hot solution cools, crystals of $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ separate. The solution of this hydrate, like lime water, is strongly alkaline in reaction and quickly becomes turbid if exposed to the air, owing to the formation of insoluble barium carbonate.

If anhydrous barium oxide be powdered and heated to redness in a tube, through which oxygen gas is passed, the latter is absorbed and the oxide BaO_2 , or barium peroxide, is formed. This is the body we have already used in the preparation of hydrogen peroxide in Experiment 78. When the peroxide is heated to a full red heat it yields up the atom of oxygen it absorbs at the lower temperature.

As we have seen, barium, strontium, and calcium, all afford peroxides ; these are the only compounds in which the metals seem to act in any other way than as diad elements, but we are not justified, *on such grounds alone*, in assigning them any higher atomicity, as each diad atom can unite with a diad *pair* of oxygen atoms.

CHAPTER XLIV.

EXPERIMENTS WITH LITHIUM AND POTASSIUM COMPOUNDS.

LITHIUM, $\text{Li}' = 7$.—This metal is commonly regarded as a rare element, for, though very widely distributed, it is met with in very small quantities. It occupies a position between the calcium, strontium, and barium group of metals and those of the alkalis, potassium and sodium. Like the latter, it is monatomic, and affords a soluble sulphate, but like the alkaline earth metals it affords a very slightly soluble carbonate and phosphate. It is met with in several mineral springs—notably in that of Wheal Clifford, in Cornwall—in *triphylline*, a phosphate with iron and manganese, and in three lithium and aluminum silicates, viz. *lepidolite*, a species of mica, *spodumene* and *petalite*. From one or other of these the carbonate, Li_2CO_3 , is prepared by methods that will be more suitably dealt with in the advanced course ; but, since the carbonate can be purchased at a moderate price, a few experiments may be made with it.

Experiment 633.—Dissolve some of the carbonate in hydrochloric acid. Carbon dioxide is evolved, and a solution is obtained which contains lithium chloride, $\text{Li}'\text{Cl}$. If the solution be evaporated to

dryness, a very deliquescent, solid residue of the anhydrous chloride is obtained which can be easily fused.

The metal lithium has been obtained by the electrolysis of the fused chloride. It is silver-white in colour, is easily oxidised in air, and is not only the element of lowest atomic weight next to hydrogen, but is the solid of lowest specific gravity, as it is only 0.59 (water=1).

Experiment 634.—Moisten a platinum wire with solution of lithium chloride and hold it in the colourless gas flame; note that a magnificent *crimson* colour is produced. This is a most convenient and delicate test for the element.

Experiment 635.—Add sodium carbonate to a strong solution of lithium chloride and warm. A white precipitate forms, and if the mixture be evaporated to dryness and the residue washed with water, LiCO_3 is obtained. This body, though slightly soluble in plain water, is very sensibly soluble in carbonic acid; and when the solution is prepared under pressure, it constitutes the 'lithia water' used in the treatment of gout.

When the carbonate is boiled with water to which sufficient slaked lime has been added to combine with all the carbonic acid of the salt, an alkaline solution is obtained which contains lithium hydrate, LiOH .

Experiment 636.—Add to a solution of lithium chloride some sodium phosphate, Na_2HPO_4 , and a few drops of caustic soda; a precipitate of Li_3PO_4 is formed, and when the mixture is evaporated and the

soluble salts washed away, the lithium phosphate is obtained in a pure state. It is the least soluble of the lithium salts, and is that commonly separated in the course of analysis. The other compounds of the element are not of sufficient importance for notice in this course.

Only two metals of common occurrence remain for consideration, namely POTASSIUM and SODIUM, while some compounds of AMMONIUM naturally find a place among the salts of the above-named 'alkali-metals.'

POTASSIUM, $K' = 39.1$.—The name of this element is derived from 'potash' or 'potashes,' as the ashes obtained on burning refuse wood, twigs, &c., in 'pots' or in pits consist in great part of potassium carbonate, resulting from the combustion of potassium salts of various organic (*i.e.*, carbon) acids present in the plant tissues.¹ The kind of change suffered by these organic salts of potassium on burning is well illustrated by

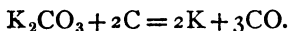
Experiment 637.—Obtain some 'cream of tartar' which is a tartrate of potassium and hydrogen, that contains $KHC_4H_4O_6$, and is the salt of an organic acid (tartaric acid) often met with in vegetable tissues. Heat some of the salt in a covered crucible until vapours are no longer evolved; the residue so obtained is black, and is a very intimate mixture of finely divided carbon and potassium carbonate. When

¹ Large quantities of potassium salts are now derived from the minerals *carnallite*, $KCl, MgCl_2, 6H_2O$; *kainite*, $K_2SO_4, MgSO_4, MgCl_2, 5H_2O$; and even from *felspar*, $K_2Al_2Si_2O_{10}$

air is admitted to the black residue, while heated to low redness, the carbon is slowly burned off, and a white 'ash' ultimately left, which consists wholly of potassium carbonate. The product is often called 'salt of tartar' if derived from 'cream of tartar' as above; this is the representative of the ash obtained on burning wood.

On the large scale the crude ash is dissolved in water, the solution filtered from unburned carbon, clay, &c., and is then evaporated to dryness. The residue is calcined, and if white is termed 'pearl ash.' Potassium carbonate is a white crystalline powder, very deliquescent and soluble in water, to which it communicates a caustic taste and strongly alkaline reaction. It is not soluble in strong spirit. The *potassæ carbonas*, B.P., which is obtained by resolution and partial crystallisation of pearl ash, contains about 16 per cent. of water, which is driven off at 130° C. This proportion of water nearly corresponds to that of a hydrate, $2K_2CO_3, 3H_2O$.

Metallic potassium is obtained by heating, in iron bottles or retorts, the mixture of potassium carbonate and finely divided carbon obtained as above from 'cream of tartar.'¹ A full white heat is required to effect the decomposition:—

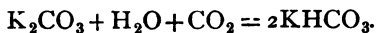


The potassium is vaporised and distils over into condensers of peculiar construction, in which it is collected

¹ It was first obtained by its discoverer, Sir Humphrey Davy, by the electrolysis of moist potassium hydrate.

and retained under naphtha, as the metal easily takes fire in air, and we already know, from Experiment 46, that water cannot be used. The metal is soft, and is usually met with in pellets. When one of these is cut, the fresh surfaces exhibit the metallic lustre, and the colour of the metal is slightly bluish white. It rapidly tarnishes in air owing to oxidation, and when thrown on water decomposes it, liberating hydrogen and affording potassium hydrate (repeat Experiment 46).

Experiment 638.—Dissolve some purified pearl ash in one and a half time its own weight of water. Pour about 10 cubic centimetres of the solution into a large flask or bottle of about a litre capacity, previously filled with carbon dioxide gas. The flask should be closed by a cork pierced by a pin in order that air may gradually flow in, for on agitating the solution with the gas absorption occurs, and air enters to supply the place of the gas absorbed. After some time the solution deposits crystals, and these consist of KHCO_3 , potassium hydrogen carbonate, or 'bicarbonate of potash,' the *potassæ bicarbonas*, B.P. If the charge of carbon dioxide gas be renewed from time to time, the whole of the normal carbonate can be converted into the new salt, which is much less soluble¹:—



The salt crystallises in trimetric prisms, which are not

¹ The normal and 'bicarbonates' are easily distinguished by means of magnesium sulphate solution, which gives with the former a white precipitate of basic magnesium carbonate, but does not precipitate the bicarbonate.

deliquescent ; the taste of the solution is but slightly alkaline, and the reaction to test-paper is also feeble. It requires about four times its weight of water for solution.

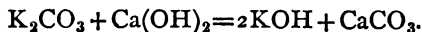
Experiment 639.—Heat to low redness, in a porcelain crucible, some crystals of the well-crystallised commercial ‘bicarbonate,’ which is generally pure ; carbon dioxide is evolved, and a residue of pure potassium carbonate is obtained. In this way the pure carbonate is easily prepared for analytical purposes.

We already know that potassium hydrate, KOH, exists,¹ and it should be possible to obtain it from the carbonate by eliminating carbon dioxide in presence of water. The readiness with which calcium hydrate combines with the carbon dioxide enables us to effect the desired change.

Experiment 640.—Dissolve some potassium carbonate in twelve parts of water, and boil the solution in a test-tube, or in a large iron vessel, if considerable quantities are operated upon. While boiling add in small successive quantities calcium hydrate or slaked lime in fine powder, stirring well after each addition. When a weight of lime has been added about equal to that of the potassium carbonate in solution, boil for a short time and let the mixture stand, in order that the precipitate may settle. When cool pour off a few drops of the clear liquid into a test-tube, and add excess of diluted hydrochloric acid. If the process has been properly conducted no effervescence will

¹ The anhydrous oxide, K_2O , can be formed on heating the metal in air ; at the same time some potassium peroxide, K_2O_2 , is produced.

follow this addition; ¹ whereas, if the white precipitate be suspended in the liquid, brisk effervescence occurs, indicating that the calcium hydrate has removed the carbon dioxide and formed a precipitate of calcium carbonate or chalk :—



The solution of potassium hydrate, or shortly *potash*, thus obtained is the *liquor potassæ*, B.P.; it is highly alkaline and corrosive. Its solution feels soapy between the fingers as it dissolves the cuticle. It cannot be filtered through paper or calico owing to its corrosive action, and must be allowed to clear from chalk by subsidence, when the solution can be poured or syphoned off. This solution rapidly absorbs carbon dioxide from the air and reforms the carbonate. If the clear solution be rapidly evaporated in a clean iron vessel, an oily liquid is ultimately obtained, a drop of which, when allowed to cool on a glass rod, becomes solid. When the liquid is in this condition and is poured into a mould of the form shown in fig. 121, it solidifies, and the stick potash, or *potassa fusa* of surgeons, is obtained. This is a very deliquescent and powerfully corrosive body. It is freely used in chemistry as a dehydrating agent, and as an absorbent of carbon dioxide gas.

Experiment 641.—Neutralise potash solution with hydrochloric acid, and evaporate the liquid until cubic crystals form; these consist of the chloride KCl. This body is found mineral as *sylvite*, and in

¹ Should effervescence occur more calcium hydrate must be added, and the liquid again boiled.

combination with magnesium chloride as *carnallite*, KCl , MgCl_2 , $6\text{H}_2\text{O}$, in large quantities at Stassfurth.

Potassium *iodide*, KI , has already been prepared in Experiment 181, the *bromide* in Experiment 195, while the *fluoride* is obtained by the method given for the corresponding sodium salt under Experiment 205.

The *hypochlorite*, KOCl , has been prepared in Experiment 151, the *chlorate*, KClO_3 , in Experiment 153, the *chromate*, K_2CrO_4 , in Experiment 528, the *bichromate* in Experiment 513, and the *permanganate* in Experiment 507.

Experiment 642.—Neutralise potash solution with nitric acid and evaporate the liquid to the crystallising point, when fine trimetric prisms separate. These consist of potassium nitrate, KNO_3 , or ‘nitre,’ as it is usually termed. The experiment is substantially a repetition of 101, which latter, with 102, should be referred to.

One of the chief uses of nitre is in the production of *gunpowder* (see Experiment 104).

Nitre, or ‘saltpetre,’¹ is met with, especially in hot and dry countries, as an efflorescence on soil in which nitrogenised organic matter has oxidised in presence of potassium compounds. Thus the soil around Indian villages affords nitre when washed with water, and a portion of the nitre of commerce is obtained in this way. But artificial nitre beds until recently afforded the chief supplies; these beds are made up of dung and some porous and calcareous earth, the *mixture* is watered with solution of wood ashes, and

¹ So named because it sometimes occurs as an efflorescence on stones.

after about two years is found to contain much nitre, which can be then extracted with water and purified by frequent crystallisation. In these cases the nitrogenised organic matter gradually decomposes¹ and ammonia results; the latter oxidises in the way indicated under Experiments 121, 122 (footnote), and calcium nitrate is formed, which affords calcium carbonate and potassium nitrate when the mass is watered with the liquid containing the potassium carbonate of wood ashes.

Much of the nitre of commerce is now obtained by the action of the crude potassium chloride on sodium nitrate—Peruvian or Chili nitre—which is obtainable in large quantities from the high table-land of Tamaragual in Peru; sodium chloride and the much less soluble potassium nitrate result from the reaction.

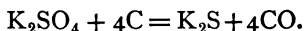
Experiment 643.—Neutralise some potash solution, or potassium carbonate, with diluted sulphuric acid, and evaporate, if necessary, until crystals begin to form. These are colourless, hard, hexagonal prisms, terminated by six-sided pyramids; they are slowly soluble in water, and require ten times their own weight for solution at ordinary temperature. They consist of K'_2SO_4 . This salt is the *potassæ sulphas*, B.P.

Since sulphuric acid is dibasic, an acid sulphate should be obtainable, thus:—

¹ It has been recently shown by Schloësing and Müntz that this process is determined by the action of minute organised ferments belonging to the group of *Micrococcus*, one of the divisions of the *Bacteria*.

Experiment 644.—Divide in two parts any quantity of dilute sulphuric acid, neutralise one part with potash as above, and add the second portion of acid ; then rapidly evaporate the liquid to a small bulk and cool the residue. If the evaporation has been carried far enough, a crystalline mass is obtained on cooling, and this has an acid taste and reaction ; it consists of the salt we are in search of, $K'H'SO''_4$. The same salt is usually obtained in fine crystals on cooling the contents of the retort after distillation of nitre with excess of sulphuric acid, as in Experiment 97.

When potassium sulphate is strongly heated with carbon in a partially closed crucible, a residue is obtained which contains the compound K_2S or potassium sulphide analogous to BaS , similarly produced in Experiment 630 :—



The K_2S dissolves in water. It can combine on heating with one, two, three, and four atoms of sulphur to form respectively the sulphides K_2S_2 , K_2S_3 , K_2S_4 , and K_2S_5 . A mixture of these sulphides with sulphate and thiosulphate forms the *potassa sulphurata*, B.P., or 'liver of sulphur,' which is thus produced:—

Experiment 645.—Mix in a small clay crucible one part of sublimed sulphur with twice its weight of potassium carbonate, and heat gradually until effervescence has ceased ; then raise the temperature *so as to fuse the product*, and pour the liquid out *on a clean stone*, cover up while cooling so as to *prevent oxidation*, and preserve the greenish-brown

mass in a stoppered bottle. Repeat Experiment 284, and so prepare solution of potassium sulphhydrate, KSH.

Experiment 646.—Hold some potassium chloride on a loop of platinum wire in the Bunsen gas flame, and note that a beautiful *violet* colour is produced. This flame test for potassium is one of great delicacy, and can be applied to any compound of the metal by moistening its powder with hydrochloric acid before heating on the wire.

Experiment 647.—Add to potassium nitrate or chloride solution a few drops of chloroplatinic acid (see p. 62), followed if necessary by some alcohol, and note that a yellow precipitate of potassium chloroplatinate is formed, K_2PtCl_6 .

Experiment 648.—Add to a *strong* solution of potassium nitrate, chloride, or other salt of the metal, a *strong* and fresh solution of *tartaric acid*, $H_2C_4H_4O_6$, and shake the mixture violently; a white crystalline precipitate soon appears. This body is the very slightly soluble potassium and hydrogen tartrate, $K'H' C_4H_4O_6$, the *potassæ tartras acida*, B.P., or 'cream of tartar,' we used in Experiment 637. This salt is the chief constituent of the crude 'tartar' that separates from wines on standing after primary fermentation.

When cream of tartar is mixed with water and sufficient potassium carbonate added to the heated mixture to neutralise the acidity of the salt, the neutral tartrate, $K_2C_4H_4O_6$, is obtained, which is wholly dissolved by its own weight of water. This very soluble tartrate is the *potassæ tartras*, B.P. For the

potassium and sodium tartrate, or *Rochelle salt*, see Experiment 656.

Potassæ acetat, B.P., $\text{KC}_2\text{H}_3\text{O}_2$, is obtained by neutralising acetic acid with potassium carbonate, evaporating until a fused product is obtained, which solidifies on cooling. The *citrate*, $\text{K}_3\text{C}_6\text{H}_5\text{O}_7$, as well as many other salts of organic acids, can be obtained by this simple method of neutralisation, but it is unnecessary to multiply experiments of this kind.

Potassium cyanide, ferrocyanide, ferricyanide, nitro-ferricyanide, and sulphocyanate, will be studied under Cyanogen Compounds in Part IV.

CHAPTER XLV.

EXPERIMENTS WITH SODIUM COMPOUNDS, AND SOME AMMONIUM SALTS.

SODIUM, Na' (*Natrium*) = 23. — Just as potassium carbonate is the ordinary source of compounds of the metal, so sodium chloride, or common salt, is the body from which the group of compounds we have now to study are derived.

In Experiment 34 we effected the synthesis of common salt,¹ NaCl, and found that it crystallised in cubes, which are soluble in about two and a half parts of water at mean temperature, and we learned from Experiment 74 that its solubility is nearly the same at a boiling temperature; contrary to the general rule, that salts are more soluble in hot than in cold liquids.

Sea water contains about 2·6 per cent. of common salt, and owes its saline taste chiefly to that body. The salt is extracted by evaporating the water and crystallising, but since the volume of water to be evaporated is very large, the operation is conducted by atmospheric agency as far as possible. Thus the sea water is allowed to trickle over piles or bundles

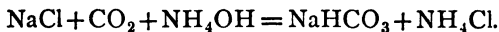
¹ The analogous iodide and bromide, as well as the hypochlorite, are prepared by the methods used for the production of the corresponding potassium salts.

of wood so as to expose a very large surface to the air, which latter, if warm and dry, rapidly evaporates much of the liquid, and a strong 'brine' is obtained that can be boiled down in shallow pans until salt separates.

Great beds of 'rock salt'—the mineral form of NaCl—occur in many parts of the world, and in these gypsum is often associated with the chloride. The best known British beds are those of Cheshire, in England, and Carrickfergus, in Ireland.

Enormous quantities of common salt are used for domestic and dietetic purposes, and as a manure in agriculture; but by far the greater part of the salt produced is employed in the manufacture of sodium carbonate, which is directly obtained in the following way :—

Experiment 649.—Shake up common salt with strong solution of ammonium hydrate; when the solution is saturated in the cold, allow the excess of salt to deposit, and pour off the clear liquid. Through the latter now pass a slow current of carbon dioxide gas; after a time a white powdery precipitate separates, which is found on analysis to consist of NaHCO_3 , while the solution contains ammonium chloride, resulting from the decomposition :—

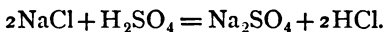


The compound deposited is 'bicarbonate of soda,' analogous to the potassium salt obtained in Experiment 638. When this body is heated it decomposes *thus* :—



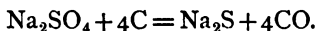
The residue is anhydrous sodium carbonate, or 'soda ash,' as it is termed when in a crude condition.

Very large and increasing quantities of common salt are converted into soda ash by this 'ammonia process,' just carried out. On the large scale the ammonia is recovered from the ammonium chloride formed in the reaction by distillation with lime; and the carbon dioxide evolved on heating the bicarbonate is used in a second decomposition of common salt, so that there is no loss theoretically; and the actual loss in practice, owing to the volatility of ammonia and other causes, has been reduced to so small an amount that the process bids fair to exclude all others for the purpose. That which has hitherto been almost exclusively used is 'Le Blanc's process,' and is named after its inventor; this method consists in the conversion of sodium chloride into sulphate as in Experiment 127; and the reduction of the latter by carbon to sulphide, which then affords sodium carbonate by decomposition with limestone. In the *first stage* of the manufacture chamber sulphuric acid is made to act on common salt in large pans, when

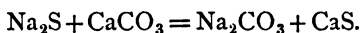


The dry sodium sulphate resulting from this treatment is termed 'salt cake,' and is ready for the next operation, while the hydrochloric acid gas is made to traverse towers filled with coke, over which a current of water trickles; the acid gas is absorbed, and the liquid that issues from the tower is used in the production of chlorine, as in Experiment 139, for the manufacture of bleaching powder and allied bodies.

The salt cake is mixed with small coal and broken limestone, and the mass is heated in a furnace which is made to revolve, whereby the materials are mixed and tolerably even heating is effected. The *second stage* in the process is the reduction of the sulphate by the carbon of the coal thus:—



The sodium sulphide thus formed then reacts with the calcium carbonate, added as limestone, and the final, or *third, stage* is reached, when



In practice more limestone is employed, in order to form an insoluble oxysulphide of calcium.

The residue of this treatment is the 'black ash,' or black ball soda, which contains some caustic soda as well as carbonate, in addition to unburned carbon, unchanged limestone, and other impurities. The extraction of the black ash by water in large tanks dissolves out the sodium carbonate and caustic alkali, while the insoluble residue forms the 'soda waste' to be seen in the neighbourhood of alkali works; the alkaline solution is evaporated to dryness in large and shallow pans, and the dry residue obtained constitutes 'soda ash.'

Experiment 650.—Dissolve the residue of the last experiment, or some common 'soda ash,' in water. Heat is evolved owing to hydration, and the *solution on* evaporation affords fine monoclinic *efflorescent crystals*, which consist of $\text{Na}_2\text{CO}_3, 10\text{H}_2\text{O}$. *This is the sodæ carbonas*, B.P., and the 'washing

soda' of commerce ; it dissolves in about six times its weight of water at ordinary temperatures.

Experiment 651.—Heat some of the crystals in a porcelain crucible, and note that they readily melt in their water of crystallisation, and part with it on continuing the heat until a dry white mass of Na_2CO_3 is obtained. This is the *sodæ carbonas exsiccata*, B.P. We have already produced the hydrogen sodium carbonate, or 'bicarbonate,' direct from the chloride in Experiment 649, but it is usually prepared on the large scale by intimately mixing two parts of powdered soda crystals,¹ or purified washing soda, with three parts of the dried or anhydrous carbonate obtained as above, and passing carbon dioxide gas over the mixture until absorption of gas ceases. The product is a white powder, which consists² chiefly of NaHCO_3 ; this is 'bread soda,' the *sodæ bicarbonas*, B.P. The solution of the latter, when pure, is distinguished from that of the normal carbonate by giving a *white* instead of a reddish precipitate with mercuric chloride ; moreover, its solution is not precipitated by magnesium sulphate.

Metallic sodium is prepared from the anhydrous carbonate by reduction with carbon at a white heat ; the method adopted is similar to that for potassium,

¹ The hydrated crystals are used to provide the hydrogen necessary to the production of the acid carbonate.

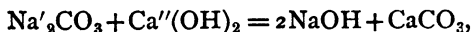
² It often contains some unchanged normal carbonate, which can be washed out by shaking the powder up with half its weight of cold water, in which the bicarbonate is slowly soluble, whereas the normal carbonate is easily dissolved and removed by draining away the liquid.

but a mixture of finely powdered charcoal or coal slack with chalk suffices, and the metal when distilled over is preserved under naphtha, as it oxidises readily. It is manufactured on a considerable scale for the reduction of aluminum and magnesium.

The metal is very soft and of a silver white colour and fine lustre, but is rapidly tarnished when exposed to the air. Its specific gravity is 0.97; its melting point is 95.7, and it is vaporised at a red heat. An alloy of sodium with potassium in atomic proportions is easily obtained by melting the metals under naphtha; this alloy is liquid at ordinary temperatures.

We already know, from Experiment 62, that sodium when burned in oxygen forms a white oxide which contains Na_2O ; this is always mixed with more or less of a higher oxide, Na_2O_2 ; the mixture forms, with water, sodium hydrate, NaOH , while a little oxygen is evolved from the higher oxide. We also know from Experiment 45 that the caustic soda is directly formed with displacement of hydrogen when the metal is thrown on water. The hydrate is, however, commonly obtained from the carbonate by the action of calcium hydrate.

Experiment 652.—Repeat Experiment 640, using sodium carbonate in seven times its weight of water instead of potassium carbonate, and conducting all the operations in the same way. The reaction,



affords the liquor sodæ, B.P., and this, on evaporation, *the solid hydrate*. This body closely resembles potas-

sium hydrate in all particulars and is the *soda caustica*, B.P.

Experiment 653.—Saturate solution of sodium hydrate with sulphuretted hydrogen gas, and warm to expel excess of gas ; the solution now contains the sulphhydrate NaSH , which is the sulphur analogue of NaOH .

Sodium nitrate, NaNO_3 , is never prepared artificially, though, like almost all other sodium salts, it can be obtained by neutralising the particular acid with caustic soda or the carbonate. It is obtained in enormous quantities from Peru and Chili. It is often termed 'Chili nitre' in allusion to its source, or 'cubic nitre' from the appearance of the crystal, but the form is that of a rhombohedron and not really of the cube. Sodium nitrate is the cheapest of all the nitrates, and is used in the sulphuric acid manufacture, in the preparation of nitric acid, and in agriculture as a manure on account of its nitrogen, but it is not employed in the production of gunpowder because it is deliquescent.

Experiment 654.—Add sodium carbonate to diluted sulphuric acid until effervescence ceases, and evaporate the solution until crystals begin to form ; when the liquid is stirred with a glass rod fine long prisms separate, which are found to consist of $\text{Na}_2\text{SO}_4, 10\text{H}_2\text{O}$, or *Glauber's salt*. The same body is obtained by dissolving 'salt cake' in water and crystallising. The salt fuses at 33° and parts with all its water at 100°C . Its maximum solubility occurs at 35° , when the crystals are readily soluble in less than their own weight of water ; this solution, if

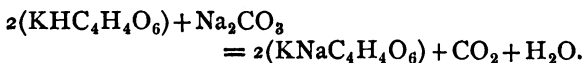
allowed to cool without disturbance, does not crystallise when cold though it is 'supersaturated,' *i.e.*, it holds in solution a much larger proportion of the salt than the water could directly dissolve at the temperature. If, however, the liquid be shaken, or a minute crystal be dropped into the solution, crystallisation rapidly occurs and the contents of the vessel become nearly solid.

Sodium sulphite, Na_2SO_3 , we have already produced in Experiment 295, and the sodium and hydrogen sulphite in Experiment 296; while we have converted the former into thiosulphate, $\text{Na}_2\text{SO}_3\text{S}$, in Experiment 312, and have noted the characters of those salts. Similarly the hypophosphite is noted under Experiment 347, the phosphates under Experiments 340, 341, and 346, the arseniate under Experiment 361, and the anhydroborate under Experiment 320.

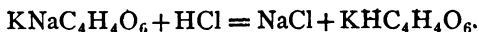
Experiment 655.—Place a few grammes of sodium carbonate in an evaporating dish with some water, heat nearly to boiling, and add acetic acid or vinegar until effervescence ceases; then evaporate until crystals form. These consist of sodium acetate, $\text{NaC}_2\text{H}_3\text{O}_2$, $3\text{H}_2\text{O}$, the *soda acetat*, B.P. The salt is prepared on the large scale by neutralising crude wood vinegar with sodium carbonate and crystallising the product.

Two tartrates of potassium were met with in Experiment 648, the normal tartrate, $\text{K}_2\text{C}_4\text{H}_4\text{O}_6$, was *shown* to result from the action of potassium carbonate on the acid salt or 'cream of tartar,' we shall now use sodium carbonate instead of the potassium salt.

Experiment 656.—Place some ‘cream of tartar’ in an evaporating dish with some water, boil, and add powdered crystals of sodium carbonate little by little, with frequent stirring, as long as effervescence occurs on further addition; filter the liquid if necessary, and evaporate the solution until crystals begin to form, and then set aside to crystallise. On cooling, beautiful transparent prisms or half-prisms separate, which have a taste like that of common salt. These consist of $\text{KNaC}_4\text{H}_4\text{O}_6, 4\text{H}_2\text{O}$, thus produced:—



This body is the *Soda Tartarata*, B.P., or ‘Rochelle Salt,’ used in Seidlitz powders. When to a strong solution of the salt some hydrochloric or acetic acid is added a precipitate of ‘cream of tartar’ is formed,



When Rochelle salt is strongly heated the organic acid is burned off, and a residue consisting of potassium and sodium carbonate in molecular proportions is left. This mixture fuses at a lower temperature than either salt alone, and is much used in analysis.

For the special antimony test for sodium, see p. 32.

Experiment 657.—Heat any sodium compound on a loop of platinum wire in the Bunsen flame. A strong and persistent *yellow* colour is produced—a reaction of extreme delicacy—in fact, it is so delicate that all bodies give this colour indication of the

presence of sodium when first plunged into a flame, as sodium is one of the most widely diffused elements.

The rare metals RUBIDIUM ($Rb' = 85$) and CÆSIUM ($Cs' = 133$) are members of the group of alkali metals, and form compounds so closely resembling those of potassium, with which they are usually associated in such small proportions that it is improbable they would have been discovered without the aid of the beautiful method of spectrum analysis; this, in the hands of Bunsen and Kirchhoff, led to their recognition in the Dürkheim mineral springs (see p. 301). They are now obtained with greater facility from lepidolite, or lithia mica, and from several similar mineral silicates.

AMMONIUM, $NH'_4 = 18$.—It was pointed out under Experiment 124 that compounds resulting from the union of ammonia gas with acids are analogous to potassium and sodium salts, and that in the saline compounds we could recognise the existence of the group NH'_4 playing the metallic rôle. We have now to notice a few of these ammonium analogues of potassium and sodium compounds not already dealt with in sufficient detail in Chapter XIV.

Experiment 658.—Neutralise some hydrochloric acid with ammonium hydrate, and evaporate the solution until crystals of 'sal ammoniac' form; these are feathery in appearance, and are made up of minute octahedra. They consist of NH_4Cl , or ammonium chloride. The salt is soluble in about three times its weight of water at mean temperature.

Experiment 659.—Heat a small quantity of dry ammonium chloride in a dry test-tube; note that it *sublimes* easily.

Ordinary sal ammoniac is obtained on the large scale by neutralising hydrochloric acid with the ammonia evolved when gas liquor is distilled with lime. The solution of the salt thus obtained is evaporated, and the dry residue then sublimed, when it is obtained in tough masses of the nearly pure salt.

The iodide, NH_4I , and bromide, NH_4Br , are prepared by neutralising the respective acids with ammonium hydrate or carbonate.

Experiment 660.—Neutralise diluted sulphuric acid with ammonium hydrate, and evaporate the solution to the crystallising point, when colourless trimetric prisms of the sulphate, $(\text{NH}_4)_2\text{SO}_4$, separate. This body when heated strongly decomposes, and therefore cannot be sublimed like the chloride.

It is prepared on the large scale in the same way as the chloride, save that it is purified by ordinary crystallisation. It is largely used as an addition to artificial manures, and is a chief source of ammonia in the arts.

Experiment 661.—Mix intimately ammonium sulphate with about twice its weight of calcium carbonate, and heat the mixture in a test-tube. A strong ammoniacal odour is developed, and a white solid sublimes, while a residue of calcium sulphate is left. Break the tube and scrape the white sublimate from the side. This when dropped into any acid effervesces, and evolves carbon dioxide gas; therefore it is a carbonate. This is the *Ammonia Carbonas*,¹ B.P., and consists of $\text{N}_4\text{H}_{16}\text{C}_3\text{O}_8$; it is not, therefore, the normal ammonium carbonate, whose formula should be

¹ The process in the large scale is the same.

$(\text{NH}_4)_2\text{CO}_3$; nor is it the acid carbonate, whose formula should be NH_4HCO_3 . When extracted with alcohol the peculiar compound $\text{NH}'_4(\text{NH}_2)\text{CO}_2$,¹ or ammonium carbamate—derived from carbamic acid, $\text{H}(\text{NH}_2)'\text{CO}_2$ —is dissolved out, and ammonium hydrogen carbonate left insoluble in the spirit. The sublimed body is therefore a mixture or compound of two molecules of the latter and one of the former, thus:—



When exposed for some time to the air the carbamate is volatilised, and the hydrogen ammonium carbonate, or 'bicarbonate,' is left; the latter is the analogue of potassium or sodium 'bicarbonate.'

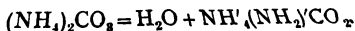
When the above sublimed carbonate is dissolved in water, and ammonium hydrate is added to the liquid, solution of the normal carbonate is obtained.

Experiment 662.—Heat ammonium chloride, or other salt, with caustic soda or slaked lime, and note that ammonia gas is evolved, which is easily recognised by its odour and its power of changing red litmus paper to blue.

Experiment 663.—Add chloroplatinic acid solution to some ammonium chloride, and note that a yellow precipitate is formed; this consists of ammonium chloroplatinate $(\text{NH}'_4)_2\text{PtCl}_6$.

Experiment 664.—Add to a strong solution of

¹ This body can be formed by the abstraction of *one* molecule of water from the normal carbonate, thus:—



If *two* molecules of water are eliminated, urea, CON_2H_4 , is obtained.

ammonium chloride a very strong solution of tartaric acid, and note that a crystalline precipitate forms, which is found to consist of $\text{NH}_4\text{HC}_4\text{H}_4\text{O}_6$, and is therefore the ammonium analogue of 'cream of tartar.' The ammonium and hydrogen tartrate is only a little more soluble than the potassium salt.

The 'Nessler test' for ammonia has been already given under Experiment 180. (See p. 100, Part II.)

The other salts of ammonium, such as the nitrate, NH_4NO_3 , the acetate, $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, the benzoate, $\text{NH}_4\text{C}_7\text{H}_5\text{O}_2$, and the phosphate, $(\text{NH}_4)_2\text{HPO}_4$, are prepared by neutralising the particular acid with ammonium hydrate, while the ammonium sodium and hydrogen phosphate, commonly called 'microcosmic salt,' has been prepared in the course of Experiment 341.

APPENDIX.

NOTE ON A CLASSIFICATION OF THE ELEMENTS.

IN the foregoing pages we have studied the elements as far as possible in the order calculated to bring into prominence their natural affinities as well as their specific differences, and have incidentally pointed out certain numerical relations between the atomic weights of certain small groups of elements, as, for instance, between those of the halogens amongst non-metals and those of the alkaline earth-metals on the electro-positive side. Relations of this kind have long been known and regarded as pointing to the existence of a connection between the atomic weight of an element and its chemical, and even physical, characters; but its nature has been only recently traced to a certain extent by Newlands in this country and Mendelejeff in Russia.

When the elements are arranged in the order of their atomic weights, and the fourteen following hydrogen are compared, the atomic weights of the analogous elements, which are those on the same horizontal line, are seen to differ by about 16. Thus:—

			Difference.
Li' = 7	. . .	Na' = 23	— 16
Be'' = 9.2	. . .	Mg'' = 24	— 14.8
B''' = 11	. . .	¹ Al''' = 27.5	— 16.5
C ^{iv} = 12	. . .	Si ^{iv} = 28	— 16
N ^v = 14	. . .	P ^v = 31	— 17
O'' = 16	. . .	S'' = 32	— 16
F' ₁ = 19	. . .	Cl' = 35.5	— 16.5

The mean difference is 16.1.

¹ Al is here represented as a pseudo-triad.

Each vertical column is a distinct series of elements rising in atomicity with increase of atomic weight from monad lithium to pentad nitrogen, and falling to diad oxygen and monad fluorine on the electro-negative side ; in the second series we have the monad sodium as the apparent homologue of lithium in the first series, and then arise to pentad phosphorus, and fall again to monad chlorine ; we thus note a *periodic* variation in chemical and other characters with increasing atomic weight, hydrogen of course being the fixed point from which this undulating system seems to proceed. Most of the other elements can be arranged in such series of similarly related bodies, together with sub-groups. Several elements are still wanting, but their probable properties can be predicted. These bodies will doubtless be discovered in time—in fact, since Mendelejeff developed the classification, several such missing bodies have been isolated, the most notable instance being that of the metal *gallium* recently discovered by Lecoq de Boisbaudran. Mendelejeff predicted the discovery of a homologue of aluminum with an atomic weight of about 68, and gallium proved to be the body required, as its atomic weight is 69·8, and its properties are between those of aluminum and indium.

The general grouping of the elements is shown in the annexed table, which is substantially that given in Watt's excellent 'Dictionary of Chemistry' (Longmans), 'Second Supplement,' p. 463, where a discussion of this subject will be found.

From the table it will be seen that the mean difference between the atomic weights of the members of the higher series is greater than that between the first two, quickly rising to 20, from $P^v = 31$ to $V^v = 51$, and then varying between 20 and 28.

Series	Group I. R ² O	Group II. RO	Group III. R ² O ³	Group IV. RH ^e RO ^a	Group V. RH ^s R ² O ^s	Group VI. RH ^s RO ^s	Group VII. RH R ² O ⁷	Group VIII. RO ^a
1	H=1							
2	Li=7	Be=9.2	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27.5	Si=28	P=31	S=32	Cl=35.5	
4	K=39	Ca=40	Sc=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63
5	(Cu=63)	Zn=65	Ga=69.8	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	Yt=89.6	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104 Pd=106, Ag=108
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	I=127	
8	Cs=133	Ba=137	La=139	Ce=141	—	—	—	
9	(—)	—	—	—	—	—	—	
10	—	—	—	—	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=197
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	

NOTE ON CRYSTALLINE FORMS.

THE various and beautiful crystalline forms assumed by salts in slowly separating either from solution, from fusion, or from the state of vapour are capable of reduction to one or other of the simple forms represented by the figures on the next page. These geometrical solids are divisible into six classes, or 'systems,' in each of which the molecules are assumed to be grouped about a special set of imaginary lines or *axes*. Each system includes prismatic and pyramidal—or open and closed—forms arranged round similar axes. Thus among the primary forms of the

1st, or *Cubic system*, are the *cube* (fig. 1*a*), or open, and the *octahedron* (fig. 1*b*), or closed form, each being grouped round three axes *a a a*, which are *equal* in length and at right angles. If we imagine the alternate faces of the octahedron to be prolonged the *tetrahedron* (fig. 1*c*) is obtained, which is, therefore, a hemi-octahedron.

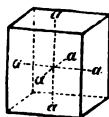
2nd, or *Square system*, in which both prism (fig. 2*a*) and pyramid (fig. 2*b*) rest on a square base; the axes are three in number and at right angles; *two* are equal, *b b*, while the third, *a*, is at right angles to their plane, and of variable length.

3rd, or *Trimetric system*, in which the prism (fig. 3*a*) and pyramid (fig. 3*b*) rest on a rectangular base, which is a parallelogram. The axes are three in number, *a b c*, rectangular, but *unequal* in length.

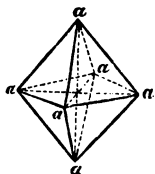
4th, or *Monoclinic system*, in which the lateral axes of prism (fig. 4*a*) and octahedron (fig. 4*b*) are at right angles, and the third is *inclined* to their plane.

5th, or *Triclinic system*, includes forms referable to a system of three axes, all of which are inclined (see figs. 5*a* and 5*b*).

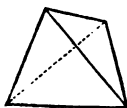
1a



1b



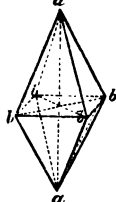
1c



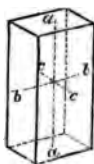
2a



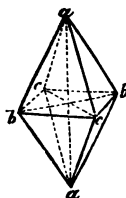
2b



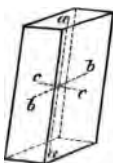
3a



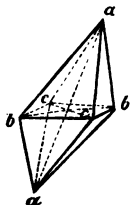
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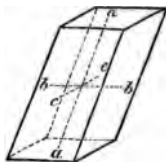
4a



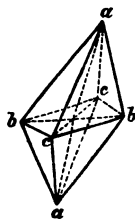
4b



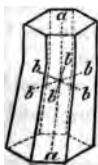
5a



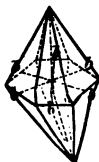
5b



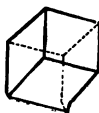
6a



6b



6c



6th, or *Hexagonal system*, in which prism (fig. 6a) and pyramid (fig. 6b) alike rest on a base which is a regular hexagon. The lateral axes are three in number, $b\ b\ b$, are situated in the same plane, and inclined at angles of 60° , while the *fourth* axis, a , is vertical to their plane. The *rhombohedron* (fig. 6c) is a hemi-pyramid of this system.

The simple forms are rarely met with unmodified ; thus the solid angles are often replaced by planes, and are then said to be *truncated*, and the edges may be either modified by a single plane or by a pair of planes ; in the latter case they are said to be *bevelled*. But our space is too limited to admit of pursuing this interesting subject here, and the reader is referred to Bauermann's 'Systematic Mineralogy' (Longmans, London) for fuller information on crystallography.

NOTE ON SPECTRUM ANALYSIS.

WHEN the light emitted by a lamp or candle flame is allowed to pass through a narrow slit and then through a glass prism held before the eye, a rainbow-coloured band is perceived. This is the expanded image of the slit resulting from the refraction and dispersion of the rays of white light transmitted, and this image is the *spectrum* of the light, and is *continuous*. Any *solid* body, when heated up to the point at which it emits light, that is sensibly white, will afford a similar continuous or uninterrupted spectrum. Consequently the latter is not characteristic of the matter heated.

If, however, we examine in the same way the bright yellow light produced when *sodium* compounds volatilise in the otherwise nearly colourless Bunsen gas flame, all

the light is seen to be concentrated on an apparently single¹ *yellow line*. On substituting a flame coloured by *lithium* the spectrum observed is very different, and consists of a single fine *bright red* line and a faint orange band. The potassium flame spectrum consists of two lines—one a dull red line, much less refrangible than that of lithium, and another at the opposite end of the spectrum of a pale *lavender* tint, with a general glow between; similarly barium gives a number of bright *green* lines, strontium several *crimson* lines and a beautiful *blue* one, while calcium gives characteristic *orange* and *green* lines. These are *interrupted* or discontinuous spectra, which are produced by incandescent *gas* or *vapour*, and are perfectly characteristic of the particular element; moreover, a very small quantity of material is capable of producing the clearly-defined spectrum. Thus, $\frac{1}{2000000}$ th of a milligram of sodium gives quite a strong spectrum, while $\frac{1}{1000000}$ th m-gr. of a lithium compound, $\frac{1}{1000}$ th of potassium, $\frac{1}{10000}$ th of strontium, $\frac{1}{1000000}$ th of calcium, and $\frac{1}{1000}$ th of barium can be detected with certainty and rapidity.

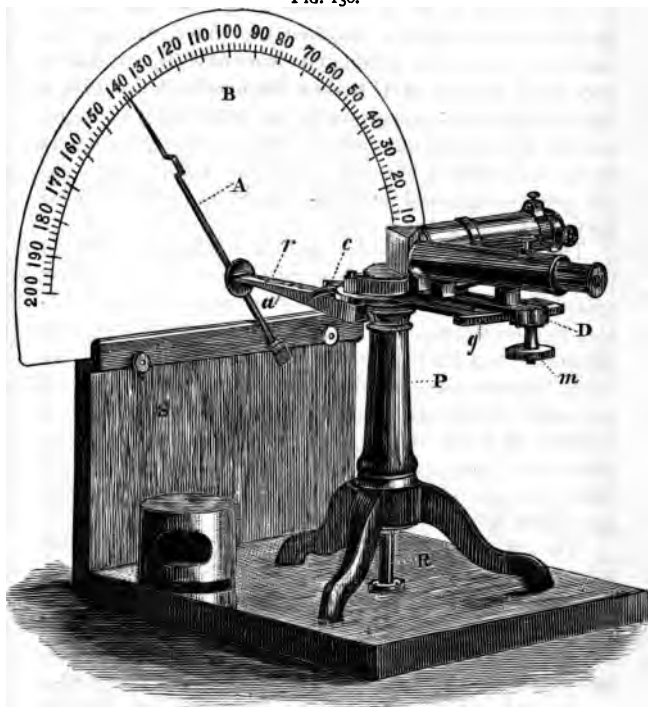
This beautiful and delicate method of analysis we owe to Professors Bunsen and Kirchhoff, of Heidelberg. The analysis of mixtures by this method does not present any difficulty, as a mixture of salts of the above metals when volatilised in the Bunsen flame affords a spectrum which includes all the lines, and the latter are easily identified by their positions and colouring; thus the qualitative analysis of complex mixtures can be made in a few seconds.

The apparatus with which observations of this kind are made is shown in fig. 136, and is termed a *spectroscope*. The instrument figured is provided with a measuring apparatus devised by the writer for the purpose of registering the positions of bright lines. D is a telescope

¹ Really a pair of fine lines.

for observing the spectrum of a flame or other source of light, the rays from which pass through a narrow slit carried by the distant end of the second telescope ; this

FIG. 136.



slit is placed in the principal focus of a convex lens, consequently the rays emergent from the latter are parallel, and thus enter the glass prism, suffering in *their course* refraction and dispersion, and affording the

spectrum observed with the telescope D. The latter is moved by means of the milled head *m* over a graduated arc, *g*, and the motion of the telescope as it appears to traverse the spectrum is transferred by means of a toothed strip, *c*, to a serrated wheel on the rod *r*, to the end of which is attached the index A, and this traverses the large graduated semicircle B, so that a very small motion of D makes the needle A describe a considerable arc; consequently the measurement of the angular distance of any sets of lines in the spectrum is easily and quickly effected. P is the pillar supporting the spectroscope, and the brass cap shown on the stand is used for covering the prism.

The metals of the alkalis and alkaline earths are those whose spectra are easily obtained by heating any of their volatile compounds—chlorides, for instance—in the colourless Bunsen flame. The spectra of other metals are best obtained when intense sparks from an induction coil are taken between poles of the particular metal or poles of platinum (whose spectrum is known), moistened with a solution of a salt of the body. The spectra of gases is obtained by observing the light emitted when sparks are taken between platinum poles in an atmosphere of the gas whose spectrum is required.

The precision and delicacy of spectrum analysis has afforded great facilities for the search after new elements, and the first fruits of work in this direction were the discovery of *cæsium* and *rubidium* by Bunsen, and, later on, of *thallium* by Crookes, *indium* by Rich and Richter, and very recently of *gallium* by Lecoq de Boisbaudran.

A work on Physics should be consulted for the application of the spectroscope to solar and stellar analysis, and to the examination of coloured fluids.

ANALYTICAL TABLES.

QUALITATIVE ANALYSIS OF METALLIC SOLUTIONS.

THE analysis of a compound with a view to the detection of its metallic constituents is conducted on the same general plan as that employed in the recognition of acids in Part II. Thus, *group* tests are used in the first instance in order to limit the area of search, then *distinguishing* reagents to indicate particular members of groups, and finally *confirmatory* tests.

In the tables which will be found at pp. 310-319 we give a synoptic view of the reactions of the metals and pseudo-metals, in order that the student may have distinctly before him the grounds on which particular tests are selected for the above purposes. It is assumed that he has already performed the experiments, and requires only the shortest indication as to the nature of the tests, and references are given to the pages on which the compounds of the particular metals are described in this part. The student is expected to compare the reactions presented in the tables in order that he may grasp the distinctive characters of the metals, and thus devise for himself schemes for their recognition and for their separation when necessary. He is provided with a distinct guide for the recognition of groups in Table I., and is aided in the selection of the tests given in Table III. which are most suitable for particular purposes by the use of special type, as specified in the footnote to Table III. As an illustration of the use to which these tables can be put we give a scheme in Table II.

for the analysis of a solution that contains only *one* metal. This table assumes that the group to which the metal belongs is known, and involves the application of a very small number of common tests which give excellent results in practice ; but it is only one of the many schemes that can be devised for the purpose by the use of the extended tables, and the student should be encouraged to plan methods for the identification of single metals, and, later on, for the examination of more or less complex mixtures, as only in this way will he become an intelligent analyst. Premising this much, we shall now shortly state the plan of analysis *for a single metal in a compound which is soluble in water.*

The first step is to *find the group* to which the metal belongs ; for this purpose proceed exactly as stated in Table I., *adding the tests in succession to the same portion of solution.* That is to say, add a few drops of HCl to the liquid ; if a precipitate forms add some more acid, in order to determine whether the precipitate redissolves in excess or not ; if re-solution does not occur a member of Group I. is present. Should no precipitate form members of Group I. of metals are absent. Now add *to the same solution* H_2S water ; if a precipitate be formed Group II. is indicated ; add *excess* of H_2S , *i.e.* until the liquid smells strongly of the gas after mixing, then note colour and refer to Table I.¹ As Group II. is a large one it is conveniently divided into two *sections*, as pointed out in the table. If H_2S fails to precipitate even on warming the liquid the members of Group II. are absent. Before applying the special test to this solution for Group III. it is essential to carry out the treatment directed in the note to the group, *viz.* to boil off H_2S ,

¹ If there is any reason to suspect the presence of As in the condition of arsenic acid, the solution must be boiled with H_2SO_4 before H_2S is added. On this point refer to Experiment 366.

next to boil with HNO_3 or a crystal of KClO_3 , and then to add NH_4Cl before mixing with *excess* of NH_4OH . If members of Group III. are not present, add at once to the alkaline liquid NH_4SH , which precipitates the members of Group IV., and if these are absent add $(\text{NH}_4)_2\text{CO}_3$ solution in order to precipitate the metals of Group V. A solution which fails to give a precipitate with any of the above general reagents can only contain members of Group VI.

In order to distinguish the metal, having first found the group to which it belongs, proceed as directed in Table II. in order to recognise the particular metal, and then completely identify it by means of the special reactions given in the succeeding tables.

In the case of a compound insoluble in water add hydrochloric acid, and heat in order to get it into solution; when dissolved the liquid must be diluted in order to avoid the probable interference of strong acid with the tests, and proceed as before, commencing with H_2S , as it is obviously unnecessary to add more HCl . If the body fails to dissolve in HCl , take a *fresh* portion and treat with HNO_3 . Should the latter dissolve the compound, dilute with water, and add to the solution the group reagents, now beginning with HCl . Some bodies fail to dissolve in either acid alone, but they pass into solution when a mixture of HCl and HNO_3 , *aqua regia*, is used. Bodies not soluble in water or acids must be fused with sodium carbonate as described in the Analytical Appendix to Part II., p. 275; the carbonate or oxide left on the filter upon extraction of the fused mass with water is dissolved in diluted hydrochloric or nitric acid, and the solution examined as above.

TABLE
DETECTION OF

GENERAL REAGENTS

GROUP I.—Hydrochloric Acid added in excess precipitates .

NOTE.—Ag and Hg (from *mercurous* compounds) are completely precipitated by HCl; Pb is not completely thrown down, owing to the slight solubility of its chloride. If Sb or Bi salts are present, HCl often produces a precipitate, but this p. dissolves in excess of the reagent. When a sulphide, or thiosulphate, is present, the liquid becomes milky on the addition of HCl, owing to the separation of S; in the former case H_2S , and in the latter SO_2 gas is evolved. Silicic acid is often separated from an alkaline solution by HCl; and 'cream of tartar' ($KHC_4H_4O_6$) from strong solutions of neutral potassium tartrate.

GROUP II.— H_2S added in excess to Solution containing HCl¹ completely precipitates

NOTE.—*Action of H_2S .* The liquid becomes milky, owing to the separation of nearly white S, if the solution contains much HNO_3 or free Cl, I, Br, SO_2 , or $HClO_3$; also, if Fe_2Cl_6 , H_2CrO_4 , or $HMnO_4$ happen to be present. The first-named bodies can usually be removed either wholly or in great part by boiling for some time with HCl; any great excess of free acid must then be neutralised by NH_4OH , and the liquid diluted before H_2S is added.

In order to distinguish the Section add to the turbid liquid, which has been boiled to expel H_2S , NH_4OH in excess. If the p. be yellow and dissolves it is probably As_2S_3 ; if not soluble add yellow NH_4SH or $NaSH$ and warm.

GROUP III.— NH_4OH added in excess precipitates completely .

NOTE.—*Before adding the group reagent*, it is absolutely necessary to boil the liquid to expel all H_2S , then to add HNO_3 or a crystal of $KClO_3$, and boil again, in order to convert any Fe present into Ferric compounds and to expel oxides of chlorine and free Cl; finally, to add NH_4Cl and NH_4OH until the solution smells strongly of the latter. The addition of NH_4Cl at this stage prevents the precipitation of Mg with the group, and prepares the liquid for the application of the general reagent for the next group. Citric and tartaric acids, sugar, and many other organic bodies prevent the precipitation of the members of this group by NH_4OH , or the other caustic alkalis.

GROUP IV.— NH_4SH added to the Alkaline Solution precipitates completely

NOTE.—If a member of the group happens to be present, take care to add but little more of the reagent than is necessary to secure complete precipitation, owing to the solubility of NiS in the Am sulphide. The NH_4Cl added in testing for the last group facilitates the separation of the sulphides of the 4th group.

GROUP V.— $(NH_4)_2CO_3$ added to Alkaline (or neutral) Solution completely precipitates

GROUP VI.—Metals not precipitated by any general reagent.

¹ The solution must not contain much free acid, and H_2S must be added until the solution, in order to promote the separation of the precipitate.

² $NaSH$ must be used if CuS be present (see p. 122). These sulphides are in excess of HCl.

I.

METALLIC GROUPS.

COMPOUNDS PRECIPITATED FROM SOLUTION BY GROUP REAGENTS

$\text{Ag}'\text{Cl}$, white.	$\text{Hg}''_2\text{Cl}_2$, white.	$\text{Pb}''\text{Cl}_2$ (slightly soluble), white.																				
<div style="display: flex; justify-content: space-between;"> <div style="width: 30%;"> <p>SECTION I.—Not dissolved by NH_4OH or yellow Am sulphide.</p> <p>SECTION II. — Dissolved on treatment of p. with NH_4OH and yellow Am sulphide.³</p> </div> <div style="width: 65%;"> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 15%; text-align: center; vertical-align: top; padding: 5px;">$\text{Cu}''\text{S}$,</td> <td style="width: 15%; text-align: center; vertical-align: top; padding: 5px;">$\text{Hg}''\text{S}$,^a</td> <td style="width: 15%; text-align: center; vertical-align: top; padding: 5px;">$\text{Bi}''_2\text{S}_3$,</td> <td style="width: 15%; text-align: center; vertical-align: top; padding: 5px;">$\text{Pb}''\text{S}$,</td> <td style="width: 15%; text-align: center; vertical-align: top; padding: 5px;">$\text{Cd}''\text{S}$, yellow.</td> </tr> <tr> <td colspan="5" style="text-align: center; padding: 5px;"> <div style="display: flex; justify-content: center; align-items: center;"> <div style="border-top: 1px solid black; width: 80%;"></div> </div> black, or brownish-black. </td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">$\text{Sb}''_2\text{S}_3$, orange.</td> <td style="text-align: center; vertical-align: top; padding: 5px;">$\text{As}'''_2\text{S}_3$,</td> <td style="text-align: center; vertical-align: top; padding: 5px;">Sn^{iv}S_2,</td> <td style="text-align: center; vertical-align: top; padding: 5px;">$\text{Sn}''\text{S}$, nearly black.</td> <td style="text-align: center; vertical-align: top; padding: 5px;">$\text{Au}'''_2\text{S}_3$,⁴ brownish.</td> </tr> <tr> <td></td> <td colspan="2" style="text-align: center; padding: 5px;"> <div style="display: flex; justify-content: center; align-items: center;"> <div style="border-top: 1px solid black; width: 80%;"></div> </div> yellow. </td> <td></td> <td style="text-align: center; vertical-align: top; padding: 5px;">PtS_2, black.</td> </tr> </table> </div> </div>			$\text{Cu}''\text{S}$,	$\text{Hg}''\text{S}$, ^a	$\text{Bi}''_2\text{S}_3$,	$\text{Pb}''\text{S}$,	$\text{Cd}''\text{S}$, yellow.	<div style="display: flex; justify-content: center; align-items: center;"> <div style="border-top: 1px solid black; width: 80%;"></div> </div> black, or brownish-black.					$\text{Sb}''_2\text{S}_3$, orange.	$\text{As}'''_2\text{S}_3$,	Sn^{iv}S_2 ,	$\text{Sn}''\text{S}$, nearly black.	$\text{Au}'''_2\text{S}_3$, ⁴ brownish.		<div style="display: flex; justify-content: center; align-items: center;"> <div style="border-top: 1px solid black; width: 80%;"></div> </div> yellow.			PtS_2 , black.
$\text{Cu}''\text{S}$,	$\text{Hg}''\text{S}$, ^a	$\text{Bi}''_2\text{S}_3$,	$\text{Pb}''\text{S}$,	$\text{Cd}''\text{S}$, yellow.																		
<div style="display: flex; justify-content: center; align-items: center;"> <div style="border-top: 1px solid black; width: 80%;"></div> </div> black, or brownish-black.																						
$\text{Sb}''_2\text{S}_3$, orange.	$\text{As}'''_2\text{S}_3$,	Sn^{iv}S_2 ,	$\text{Sn}''\text{S}$, nearly black.	$\text{Au}'''_2\text{S}_3$, ⁴ brownish.																		
	<div style="display: flex; justify-content: center; align-items: center;"> <div style="border-top: 1px solid black; width: 80%;"></div> </div> yellow.			PtS_2 , black.																		
$\text{Fe}^{vi}_2(\text{OH})_6$, brown.	$\text{Al}^{vi}_2(\text{OH})_6$, white, translucent.	$\text{Cr}^{vi}_2(\text{OH})_6$, greenish or bluish.																				
[Or earthy salts.]																						
$\text{Co}''\text{S}$,	$\text{Ni}''\text{S}$,	$\text{Mn}''\text{S}$, buff-coloured ; quickly becomes grey on exposure to the air.																				
<div style="display: flex; justify-content: center; align-items: center;"> <div style="border-top: 1px solid black; width: 80%;"></div> </div> black.		$\text{Zn}''\text{S}$, white.																				
$\text{Ba}''\text{CO}_3$,	$\text{Sr}''\text{CO}_3$,	$\text{Ca}''\text{CO}_3$,																				
<div style="display: flex; justify-content: center; align-items: center;"> <div style="border-top: 1px solid black; width: 90%;"></div> </div> white.																						
Mg'' ,	$\text{NH}'_4(?)$	K' ,																				
		Na' ,																				
		Li' .																				

liquid *smells strongly* of the gas after violent shaking ; it is then always well to warm.
^a The Hg of *mercuric* compounds.

reprecipitated (together with S) when the solution in alkaline sulphide is treat

⁴ If the solution be warm, a black sulphide is precipitated.

TABLE

SCHEME FOR THE DETECTION OF THE
AQUEOUS

*Having ascertained with certainty, according to TABLE I., the
tions given below for the distinction of the particular*

GROUP I.—Ag, Hg⁺, (ous), Pb⁺.

Shake the white p. produced by the Group reagent (HCl) with NH₄OH.

If blackened, Hg⁺ , present.	If dissolved, Ag present.	If apparently unaffected, Pb present.
---	-------------------------------------	---

N.B.—In the above, and all similar cases, the Student is recommended to confirm his result by the application to the *original* solution of some of the more important special tests given in Table III.

GROUP II., 1st Section—Cu⁺, Hg⁺⁺(ic), Bi⁺⁺⁺, Pb⁺, Cd⁺⁺.

If the p. by Group reagent (H₂S) is yellow, **Cd** is present.

If black or brown, can only be due to the presence of Cu, Bi, Hg, or Pb.
In order to distinguish between these, add to the *original solution*
excess of Na₂CO₃—

If a greenish blue p., which darkens on boiling, Cu .	If a reddish p. forms, Hg(ic) .	If a white p., either Bi or Pb present In order to distinguish between these metals, use the SnCl ₂ and NaOH test given at p. 45.
--	---	--

2nd Section—Sb, As, Sn (-ous and -ic).¹

If yellow and soluble in NH₄OH alone,² **As** present.

If the p. by Group reagent (H₂S) is orange coloured, **Sb** is present.

If yellow, and insoluble in NH₄OH, **Sn (ic)**.

If black, **Sn** (from stannous salt).

¹ Gold and platinum excluded.

² Care must be taken to boil off H₂S before adding the ammonia.

II.

METALLIC BASE OF A SIMPLE SALT IN SOLUTION.

GROUP to which the Metal belongs, refer at once to the Director of the Group which is present in solution.

GROUP IIL.—Fe, Cr, Al.

If p. by Group reagent is brown—Fe present.

If greenish or bluish—Cr present.

If white—Al.

N.B.—If Mn be present, a little is thrown down in this place as a very dark brown p., if the oxides of Cl have not been thoroughly boiled off.

GROUP IV.—Zn'', Mn'', Co'', Ni''.

If p. by Group reagent (NH₄SH in alkaline solution) is white—Zn present.

If buff-coloured, quickly becoming grey and brown—Mn present.

If black—Co or Ni. To distinguish, add to *original solution* excess of Na₂CO₃—

If light green p., Ni.

If a light blue p., Co.

GROUP V.—Ca'', Ba'', Sr''.

Add to some of the *original solution*, CaSO₄ in saturated solution.

A white p. produced <i>immediately</i> , Ba.	A white p. formed only after some time, Sr.	No p. Ca.
		Confirm by adding to another portion of the original solution, NH ₄ OH and (NH ₄) ₂ C ₂ O ₄ .

GROUP VI.—Mg'', NH', K', Na', Li'.

Test separate portions of the *original solution* in the following order—

1. With Na₂HPO₄ and NH₄OH for Mg.
2. By boiling with NaOH for NH₃.
3. By addition of excess of strong solution of H₂C₄H₄O₆ to concentrated liquid for K.
4. By evaporating a few drops of the solution nearly to dryness, and holding a Pt wire moistened with the liquid in the Bunsen flame:—

(a) a crimson colour is given to the flame, Li;

(b) a strong and persistent yellow tint, Na.

TABLE

REACTIONS OF
GROUP I.—Metals precipitated as Chlorides

Name of Metal, &c.	HCl	NH ₄ OH on chloride	H ₂ S	KI
SILVER Pages 78-89	White curdy p.	DISSOLVED, and reprecipitated by HNO ₃	Black p.	Pale yellow p.
MERCURY (Mercurous Compounds) Pages 90-109	White p.	BLACKENED	Black p.	Greenish p.
LEAD Pages 126-142	White p., soluble in boiling water	UNCHANGED, apparently	Black p.	Bright yellow p., soluble in boiling water

GROUP II.—Metals precipitated as Sulphides from Acid
NH₄OH and Yellow

Name of Metal, &c.	H ₂ S in acid solution	NH ₄ OH in excess	Na ₂ CO ₃
MERCURY (Mercuric Compounds) Pages 90-109	P. is first white, then yellow, brown, and ultimately black; p., when well washed, is insoluble in HNO ₃ , but is dissolved by aqua regia	White p.	REDDISH BROWN P.
LEAD Pages 126-142	Black p., partially soluble with separation of S in HNO ₃ (dilute)	White p.	White p.
COPPER Pages 110-125	Brownish black p., soluble in HNO ₃ with separation of S (slightly soluble in Am sulphide, but not in NaSH)	BEAUTIFUL BLUE solution	LIGHT BLUE P., becomes nearly black on boiling mixture

NOTE.—A reaction partially printed in **thick type** is that with the group reagent. From the other members of its group is printed in SMALL CAPITALS. The most distinctions useful in working out analytical problems.

III.

METALS IN SOLUTION.

on the addition of HCl in excess.

K_2CrO_4	H_2SO_4	Na_2CO_3	Cu strip or a bright coin	Special Characters, including blowpipe reactions
<i>Brick-red p. easily soluble in acid</i>	No p. in dilute solutions	Yellowish white p.	Grey stain, not volatile on heating	<i>Ag compounds blacken</i> when exposed to light, especially in contact with organic matter
Reddish yellow p.	Ditto	<i>Dirty yellow p.</i> , changing to black	<i>Grey stain</i> , easily volatilised by heat	<i>All Hg compounds yield</i> globules of Hg when heated with dry Na_2CO_3 in a tube closed at one end
<i>Bright yellow p.</i>	WHITE P., insoluble in dilute H_2SO_4	White p.	No stain	Pb compounds easily yield metallic globules when heated on charcoal in the reducing flame of blowpipe

Solutions by H_2S .—Section I.—Sulphides insoluble in NH_4SH or $NaSH$.

KI	NaOH	K_4FeCy_6	$SnCl_2$ and NaOH in excess	Special Characters
<i>Scarlet p.</i> , easily soluble in excess of reagent	Yellowish brown p. when in excess	Yellowish white p.	Black or grey	$SnCl_2$ ALONE ADDED TO SOLUTION free from oxidising bodies gives a ppt. of Hg_2Cl_2
<i>Bright yellow p.</i>	White p., soluble in excess	White p.	White p.	As in Group I.
White p. mixed with I.	<i>Light blue p.</i> , becomes black on boiling. Insoluble in excess	<i>Reddish brown p.</i>	Bluish green p.	<i>Fe (a knife blade) precipitates Cu</i> from its acid and neutral solutions

A reaction which is specially useful in separating or distinguishing a particular metal important confirmatory reactions are indicated by italics. Students will find these

GROUP II.—

Name of Metal, &c.	H ₂ S in acid solution	NH ₄ OH in excess	Na ₂ CO ₃
CADMIUM Pages 243-244	Yellow p. , soluble in boiling dilute H ₂ SO ₄ , unlike other sulphides of the group	WHITE p. , easily soluble in excess to colourless liquid	White p.
BISMUTH Pages 38-46	Black p. , soluble in boiling HNO ₃	WHITE p. , insoluble in excess	White p.

GROUP II. (continued).—Section II.—Sulphides

Name of Metal, &c.	H ₂ S in acid solution	NH ₄ OH in excess	CuSO ₄ , 4NH ₃
ARSENIC (<i>Arsenious Compounds</i>) Pages 1-22	Yellow p. , insoluble in strong and boiling HCl. Soluble in NH ₄ OH	No p., unless arsenite insoluble in reagent is present	<i>Green p.</i> (Scheele's green)
ARSENIC (<i>Arsenic Compounds</i>) Pages 9-22	S separates first , yellow As ₂ S ₃ only after boiling with H ₂ SO ₄	No p. unless arseniate insoluble in reagent is present	Greenish blue p.
ANTIMONY Pages 25-37	Orange-red p. , easily soluble in strong and boiling HCl. Insoluble in NH ₄ OH	<i>White p.</i> almost insoluble in excess	White p., due to NH ₄ OH
TIN (<i>Stannous Compounds</i>) Pages 48-58	Brownish black p. , not dissolved by NH ₄ SH unless free S is present	White p., insoluble in excess	P. only due to NH ₄ OH
TIN (<i>Stannic Compounds</i>) Pages 48-58	Yellow p. Insoluble in (NH ₄) ₂ CO ₃	Same	P. only due to NH ₄ OH

Section I. (continued).

KI	NaOH	K_2FeCy_6	$SnCl_2$ and NaOH in excess	Special Characters
No p.	White p., insoluble in excess	White p.	White p.	<i>Cd compounds heated on C in reducing flame of blowpipe produces a brown incrustation</i>
I almost always separated	White p., insoluble in excess	White p.	BLACK P.	<i>All Bi salts, except those containing organic acids, yield white basic compounds on addition of much water</i>

soluble in NH_4SH or $NaSH$.

$AgNO_3, 2NH_3$	Cu in acid solution	Zn and H_2SO_4	Special Characters
<i>Yellow p.</i>	<i>Grey metallic coating, easily volatilised by heat in a tube closed at one end; As or crystals of As_2O_3 sublime</i>	<i>AsH_3 evolved. Burning gas deposits black stain of As on porcelain, soluble in NaClO</i>	<i>AsH_3 gas in dilute $AgNO_3$ gives a black p. of Ag. Heated with C in a tube As sublimes, garlic odour</i>
<i>Reddish brown p.</i>	<i>As last, only pptes. when solution contains large quantities of HCl</i>	Same	<i>Arsenites give a white crystalline p. with magnesia mixture</i>
No definite result. White p. in solution of tartrate and chloride	<i>Grey metallic p., not volatile, but easily soluble in KOH and $KMnO_4$</i>	<i>SbH_3 evolved. Burning gas deposits a black stain on porcelain; insoluble in NaClO, but soluble in yellow sulphide of ammonium</i>	<i>SbH_3 in dilute $AgNO_3$ gives black p. of Ag_3Sb. Solid compounds heated on charcoal globules of brittle Sb separate</i>
$SnCl_2$ gives a grey white p.	Cu somewhat discoloured	Metallic Sn separates	<i>$AuCl_3$ gives a blue or purple p. or coloration (purple of Cassius). $HgCl_2$ a white p. of Hg_2Cl_2. On charcoal with Na_2CO_3, or with KCN bead of malleable Sn obtained</i>
<i>White p. with chloride</i>	Same	Same	—

GROUP II.—

Name of Metal, &c.	H ₂ S in acid solution	NH ₄ OH in excess	CuSO ₄ , 4NH ₃
GOLD Pages 68-74	Blackish brown p., slowly formed. Insoluble in HCl	A reddish-yellow p. in strong solutions. <i>P. of fulminating gold</i>	Like NH ₄ OH
PLATINUM Pages 60-67	Brownish black p., slowly formed. Insoluble in HCl	YELLOW CRYSTALLINE P., especially if HCl be present	Acts like NH ₄ OH

GROUP III.—Metals precipitated as Hydrates, in presence of HNO₃, or KClO₃, in order to convert

Name of Metal, &c.	H ₂ S in HCl solution	NH ₄ SH in nearly neutral solution	NH ₄ OH	NaOH
IRON (<i>Ferrous Compounds</i>) Pages 172-205	No p.	<i>Black p.</i>	Nearly white p., at first, becomes greenish, then reddish brown	Same as NH ₄ OH
IRON (<i>Ferric Compounds</i>) Pages 172-205	<i>P. of sulphur</i>	<i>Black p.</i>	Foxy red p. , or reddish brown p.	Same as NH ₄ OH
ALUMINUM Pages 221-235	No p.	<i>White p.</i>	White p. , slightly soluble in great excess	WHITE P. , easily soluble in excess. Re-precipitated by NH ₄ Cl
CHROMIUM (<i>basic</i>) Pages 157-171	<i>No p. In solutions of chromates S separates, and the liquid becomes green</i>	<i>Greenish p.</i>	A greenish or bluish p. , slightly soluble in great excess	A GREENISH or bluish p. , easily soluble in excess if in the cold. The Cr is reprecipitated by boiling for a long time

¹ The Student must bear in mind that certain earthy, and alkaline earthy phosphates. When these bodies are suspected their acid radicles can be tested for in Appendix, Part II., p. 275. Moreover, in dealing with a mixed solution, a little Mr

Group II. (continued).

$\text{O}_2, 2\text{NH}_3$	Cu in acid solution	Zn and H_2SO_4	Special Characters
H_2 be tested, white p. of 1 results	<i>Au reduced</i>	<i>Au reduced</i>	FeSO_4 QUICKLY REDUCES Au from solution as a brownish p. SnCl_2 containing a little SnCl_4 gives a purple or brownish p. of 'purple of Cassius.' Oxalic acid reduces Au with facility.
red p. of 1 and the onium comd.	<i>Pt reduced</i>	<i>Pt reduced</i>	FeSO_4 solution only precipitates Pt after long boiling

H_2Cl , by excess of NH_4OH , after boiling the Acid Solution present wholly into Ferric Compounds.¹

CO_2	K_4FeCy_6	$\text{K}_3\text{Fe}_2\text{Cy}_{12}$	BaCO_3	Special Characters
1 p., ing to , and ately own	WHITE P., which quickly becomes blue	<i>Deep blue p.</i>	Ferrous salts, except FeSO_4 , not precipitated in the cold	The compounds in borax bead give greenish or yellow colours
H_2OH	RICH BLUE P.	<i>Brownish coloration</i>	Foxy red p. Separation complete in cold	KCNS gives a fine blood-red colour with ferric salts
1 p., TLY e in s	No p.	No p.	White p. Separation complete in cold	<i>Al salts strongly heated on charcoal, then moistened with solution of CoCl_2, and again heated, become blue</i>
sh p., ly so- in ex-	No p.	No p.	Greenish or bluish p. Separation complete in cold	<i>A Cr compound heated with Na_2CO_3 and KClO_3 (dry) gives a yellow mass, which, when dissolved in water and acidified with acetic acid, gives a yellow p. with $\text{Pb}''(\text{Ac})_2$</i>

oxalates, fluorides, &c., may be precipitated with the members of the group portions of the group p., and, if present, can be separated as directed in the ant, thrown down with the metals of Group III.

GROUP IV.—Metals precipitated as Sulphides by NH_4SH

Name of Metal, &c.	H_2S in HCl solution	NH_4SH in nearly neutral solution	NH_4OH	NaOH
COBALT Pages 207-214	No p.	Black p.	Blue p., soluble in excess	Blue p., insoluble in excess; it becomes reddish on boiling
NICKEL Pages 215-220	No p.	Black p., NiS somewhat soluble in excess of NH_4SH	Slight greenish p., easily soluble in excess	Greenish p., insoluble in excess
ZINC Pages 237-242	No p. If the free acid present is acetic, the Zn is completely precipitated	White p., insoluble in dilute acetic acid	White p., soluble in excess; NH_4SH gives a white p. in this solution	WHITE P., soluble in excess; H_2S gives a white p. in this solution
MANGANESE Pages 144-156	No p. unless permanganates or manganates are present, then S separates	Salmon-coloured p., passing rapidly to grey or brown	White p., becoming brown on exposure to air. Soluble in excess if NH_4Cl be present	SAME AS NH_4OH

NOTE.—The presence of many organic bodies in solution seriously interferes with Groups III. and IV. They can usually be removed by evaporation and ignition of

Solutions containing NH_4Cl and free NH_4OH .

Na_2CO_3	K_4FeCy_6	$\text{K}_4\text{Fe}_2\text{Cy}_{12}$	KCN	Special Characters
USE P.	Green p., insoluble in HCl	Brownish red p., insoluble in HCl	<i>Brownish white p., easily soluble in excess. Solution after boiling gives no p. with NaClO</i>	<i>Borax bead, coloured a beautiful blue in O flame of blowpipe</i>
FINISH P.	Greenish white p., insoluble in HCl	Yellowish brown p., insoluble in HCl	<i>Yellowish green p., easily soluble in excess. The solution boiled with NaClO gives a black p. of $\text{Ni}_2(\text{OH})_6$</i>	<i>Borax bead, coloured in O flame violet; reddish brown when cold; bead becomes grey in R flame</i>
USE P., insoluble in solution on heating	White p., insoluble in HCl	Brownish yellow p., soluble in HCl	White p., soluble in excess, and in acetic acid	<i>Zn salts heated strongly, and then moistened with CoCl_2, and again heated, become green. Heated strongly on C, Zn salts give an incrustation which is yellow when hot and white when cold</i>
USE P., coming down	Reddish white p., soluble in HCl	Brown p., insoluble in HCl (dilute)	White p., soluble in excess, and in acetic acid	<i>Borax bead, coloured violet red in O flame. Decolorised in R flame. Heated with Na_2CO_3 and KNO_3 gives a green mass</i>

actions of the alkaline hydrates and carbonates with solutions of the metals of the residue, which latter is then to be dissolved in HCl and tested as usual.

GROUP V.—Metals precipitated as Carbonate

Name of Metal, &c.	$(\text{NH}_4)_2\text{CO}_3$	CaSO_4 , saturated solution	K_2CrO_4 in neutral solution
BARIUM Pages 263-267	White p.	WHITE P. <i>immediately</i>	<i>Bright yellow p.</i> easily soluble in HCl and HNO_3
STRONTIUM Pages 261-263	White p.	WHITE P. after some time	No p.
CALCIUM Pages 251-261	White p.	No p. H_2SO_4 gives a white p. with a rather strong solution of Ca	No p.

GROUP VI.—Metals not precipi

Name of Metal, &c.	Na_2HPO_4 , with free NH_4OH	Na_2CO_3	NaOH
MAGNESIUM Pages 245-250	WHITE CRYSTAL-LINE P.	White p. No reaction in presence of Am salts	White p.
AMMONIUM Pages 289-292	No p.	No p.	NH_3 is evolved
POTASSIUM Pages 270-279	No p.	No p.	No p.
SODIUM Pages 280-288	No p.	No p.	No p.
LITHIUM Pages 268-270	A white p. in hot and strong solutions	White p. in strong solutions	No p.

by $(\text{NH}_4)_2\text{CO}_3$ from Neutral Solutions.

$(\text{NH}_4)_2\text{C}_2\text{O}_4$	$(\text{NH}_4)_2\text{SO}_4$	Special Characters
White p. Soluble in oxalic and acetic acids, in addition to mineral acids	White p., not dissolved by boiling with excess	<i>Most Ba salts, moistened with HCl, colour the flame greenish. H_2SiF_6 gives COLOURLESS CRYSTALLINE P., increased by addition of alcohol</i>
White p. Soluble in HCl and HNO_3 ; but slightly soluble in oxalic or acetic acid	White p., not dissolved by boiling with excess	<i>Sr salts give intense red colour to flame. SrSO_4 is converted into carbonate by boiling with solution of two parts of K_2CO_3 and one part of K_2SO_4. BaSO_4 is not so acted upon</i>
WHITE P. Soluble in mineral acids, but not in oxalic or acetic acid	WHITE P. Soluble in excess on boiling	<i>Ca salts communicate an orange-yellow tint to flame</i>

tated by any general Reagent.

$\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ in excess	H_2PtCl_6 and alcohol	$\text{Ba}(\text{OH})_2$	Special Characters
No p.	—	WHITE P. The precipitation is complete	<i>MgO moistened with CoCl_2 solution, and heated on C, assumes a pinkish colour</i>
WHITE CRYSTALLINE P.	YELLOW P.	NH_3 is evolved	<i>Nessler's test (an alkaline solution of HgI_2 in KI) gives a strong brown p., or brownish yellow coloration with Am salts</i>
WHITE CRYSTALLINE P.	YELLOW P.	No p.	<i>K salts colour the flame violet</i>
No p.	No p.	No p.	<i>Na salts colour the flame yellow</i>
No p.	No p.	—	<i>LI SALTS COLOUR THE FLAME crimson</i>

LONDON : PRINTED BY
SPOTTISWOODE AND CO., NEW-STREET SQUARE
AND PARLIAMENT STREET

